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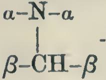
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JOURNAL

OF

THE CHEMICAL SOCIETY.

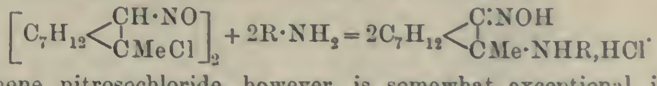
TRANSACTIONS.

I.—*Pinene Nitrolamine.*

By **Frederick Peacock Leach.**

Attention has been drawn to the fact that ammonia reacts with pinene nitrosochloride, producing a well-defined amino-oxime by the replacement of the chlorine by the amino-group (Proc., 1906, **22**, 137). The present communication deals with the preparation and properties of this substance, which is shown to possess the character of a primary amine as well as that of an oxime.

It is well known that the nitrosochlorides of the terpenes, when treated with a primary or secondary amine, give rise to nitrolamines, the chlorine being replaced by the basic residue with formation of the hydrochloride of the base, accompanied by resolution of the bis-nitroso-linking and the formation of an oximino-group:



$$\left[\mathrm{C_7H_{12}}<\begin{array}{l}\mathrm{CH\cdot NO}\\ \mid\\ \mathrm{CMeCl}\end{array}\right]_2 + \mathrm{2R\cdot NH_2} = \mathrm{2C_7H_{12}}<\begin{array}{l}\mathrm{C{:}NOH}\\ \mid\\ \mathrm{CMe\cdot NHR,HCl}\end{array}$$

Pinene nitrosochloride, however, is somewhat exceptional in its behaviour towards primary and secondary amines; towards aliphatic amines it reacts quite normally, but with an aromatic amine such as aniline, the elements of nitrosyl chloride are withdrawn, inactive pinene and aminoazobenzene hydrochloride being formed:

$$\mathrm{C_{10}H_{16}\cdot NOCl + 2C_6H_5\cdot NH_2 = C_{10}H_{16} + C_6H_5\cdot N{:}N\cdot C_6H_4\cdot NH_2,HCl + H_2O.}$$

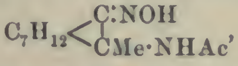
The interest attaching to this reaction depends on the demonstration that when nitrosyl chloride is added to pinene no secondary reaction takes place such as occurs when hydrogen chloride is added to the hydrocarbon, although the nitrosochloride is optically inactive (compare Armstrong, Trans., 1896, **69**, 1400).

The production of the substituted nitrolamines from many terpene nitrosochlorides has been widely studied by Wallach and his co-workers, but hitherto the original nitrolamine bases themselves have not been obtained, except in the case of pinole nitrosochloride, $[C_{10}H_{16}O{\cdot}NOCl]_2$ or $C_{10}H_{16}O{\cdot}NOCl$, which gives the nitrolamine when treated with alcoholic ammonia (*Annalen*, 1889, **253**, 262). It therefore seemed desirable, particularly in the case of pinene, to obtain the nitrolamine base, because on reduction one might expect to produce the corresponding diamine, which when treated with nitrous acid should give a glycol identical with that obtained by G. Wagner (*Ber.*, 1894, **27**, 2270) on oxidising the hydrocarbon by means of a 1 per cent. solution of potassium permanganate at 0°, whilst if the glycol could be obtained with any degree of ease it could be made the starting-point for useful work in connexion with the pinene nucleus.

It was shown in the case of the reaction between the limonene nitrosochlorides and potassium cyanide that temperature had a very marked influence on the course of the reaction (Trans., 1905, **87**, 417); at the boiling point of alcohol, little or no nitrosocyanide was produced, whilst at about 25—30° the yield approximated to 30 per cent. It therefore seemed probable that the reaction between pinene nitrosochloride and ammonia might be influenced in the same way; this proves to be the case, for when ammonia in alcoholic solution is boiled with pinene nitrosochloride, hydrochloric acid is withdrawn and a brown, resinous mass obtained, from which only small quantities of nitrosopinene (melting at 131°) could be extracted. If, however, the nitrosochloride is ground to a fine powder and suspended in absolute alcohol, concentrated ammonia added, and the solution maintained at 45° with occasional shaking, the reaction proceeds slowly, the nitrosochloride disappears, and an almost colourless solution is formed, from which, on pouring into water, the nitrolamine is precipitated in bulky, white needles. The yield is almost quantitative, and the success of the operation can usually be judged by the colour of the solution, a brown colour indicating destruction of the nitrosochloride and a diminished yield of the nitrolamine.

Pinene nitrolamine is amphoteric in character, dissolving readily either in dilute caustic alkali or in dilute acids; it possesses the properties of a primary amine, giving rise to a well-defined hydrochloride, oxalate, and platinichloride. The nitrolamine yields an unstable *iso*nitrile and condenses readily with aldehydes to form crystalline condensation derivatives.

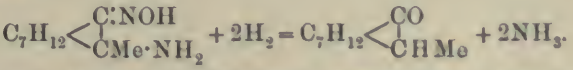
Acetic anhydride gives rise to a monoacetyl derivative,



$$\mathrm{C_7H_{12}}<\begin{array}{l}\mathrm{C{:}NOH}\\ \mathrm{CMe{\cdot}NHAc}\end{array},$$

which is soluble in alkalis, but attempts to prepare a diacetyl derivative led to the production of a black tar. Well-defined dibenzoyl and diphenylcarbamide compounds have, however, been prepared.

The chief interest lay in the action of reducing agents, but hitherto disappointing results have been obtained. With boiling amyl or ethyl alcohol and sodium, 90 per cent. of the nitrolamine was recovered unchanged, whilst with acid reducing agents there was either no reduction or else the amino-groups were eliminated, giving rise to a ketone (Wallach's pinocamphone). Dilute or glacial acetic acid and zinc dust had no effect on the nitrolamine, almost the whole of the substance being recovered unchanged, but with alcoholic hydrochloric acid and zinc dust (below 50°), 60 per cent. was recovered, the principal reduction product being pinocamphone, identified by means of its oxime.



$$\mathrm{C_7H_{12}}<\begin{array}{l}\mathrm{C{:}NOH}\\ \mathrm{CMe{\cdot}NH_2}\end{array} + 2\mathrm{H_2} = \mathrm{C_7H_{12}}<\begin{array}{l}\mathrm{CO}\\ \mathrm{CHMe}\end{array} + 2\mathrm{NH_3}.$$

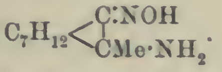
This result agrees with Wallach's observations, who found that when nitrosopinene is reduced with zinc dust and dilute acetic acid, the base, pinylamine, is obtained, mixed with about 20 per cent. of pinocamphone (*Annalen*, 1898, **300**, 287).

The corresponding amino-oxime of camphor was prepared by Lapworth (Trans., 1902, **81**, 549), by the action of hydroxylamine acetate on aminocamphor, which on reduction with sodium and alcohol gives rise to bornylenediamine (P. Duden, D.R.-P. 160103). The behaviour of the pinene compound on reduction emphasises the difference between the two substances.

Pinene nitrolamine is optically inactive, as would be expected, on account of its derivation from pinene nitrosochloride.

EXPERIMENTAL.

Pinene nitrolamine, $\mathrm{C_7H_{12}}<\begin{array}{l}\mathrm{C{:}NOH}\\ \mathrm{CMe{\cdot}NH_2}\end{array}$.



Twenty grams of pinene nitrosochloride were ground to a fine powder and suspended in 100 c.c. of absolute alcohol; 25 c.c. of concentrated ammonia were added and the mixture kept at a temperature of 45° with occasional shaking. The nitrosochloride gradually disappeared, an almost colourless solution being formed, from which, on cooling, there separated a solid mass of the nitrolamine mixed with some ammonium chloride. On filtering, washing with water, and crystallising from hot alcohol a pure product was obtained. The alcoholic solution from the reaction was poured into a large volume of water, giving a very bulky mass of fine needles, and after filtration and recrystallisation from hot alcohol a further supply of the nitrolamine was produced; this compound, which crystallised in long, silky needles, melted at 123—125°, and softened at 117°. Further recrystallisation did not alter the melting point, but on fusion gas was evolved and the substance again melted at 129—131°.

The most probable explanation appeared to be the formation of nitrosopinene (m.p. 131°) from the nitrolamine by evolution of ammonia. On mixing a small quantity of the fused substance with nitrosopinene, the mixture began to melt below 100°, whilst the molten substance itself dissolved completely in dilute hydrochloric acid, from which the original nitrolamine melting at 123—125° was precipitated by the addition of ammonia:

0·1111 gave 0·2548 CO_2 and 0·0992 H_2O. C = 62·54; H = 9·92.
0·1160 ,, 14·8 c.c. moist nitrogen at 21° and 766 mm. N = 14·64.
$C_{10}H_{18}ON_2$ requires C = 65·9; H = 9·88; N = 15·38.
$C_{10}H_{18}ON_2,\frac{1}{2}H_2O$,, C = 62·82; H = 9·94; N = 14·66 per cent.

When heated in a dry test-tube, the substance melts and moisture collects on the upper part of the tube; its direct estimation by heating at 100° is frustrated owing to the fact that sublimation takes place. Heated in the water-oven, the crystals lose their lustre and transparent appearance, becoming quite opaque. At the surface of the layer, small, brilliant plates sublime, and after the heating has been continued for several hours and the product recrystallised from hot light petroleum, small tufts of silky needles are produced melting sharply at 137°:

0·1332 gave 0·3154 CO_2 and 0·1180 H_2O. C = 64·57; H = 9·84.
$C_{10}H_{18}ON_2$ requires C = 65·9; H = 9·88.

The nitrolamine dissolves readily in dilute mineral acids, being reprecipitated unchanged by ammonia as a bulky mass of fine needles; it also dissolves in dilute caustic alkalis. From hot alcohol, chloroform, or acetic acid it crystallises in fine, silky needles; it is moderately soluble in warm benzene, acetone, or light petroleum, but very sparingly so in ether. It is not readily attacked on boiling with dilute hydrochloric acid, the hydrochloride separating out on cooling; prolonged boiling, however, causes elimination of the oximino-group, and, on addition of caustic soda and Fehling's solution, a red precipitate of cuprous oxide is produced.

Action of Bromine.—A solution of the nitrolamine in chloroform decolorises bromine, and almost immediately a bulky, white, crystalline precipitate separates. After filtration and washing with a little chloroform, it is snow-white and stable in the air, but dissolves completely in water with elimination of hydrobromic acid and regeneration of the nitrolamine.

Action of 30 *per cent. Aqueous Alkali.*—When boiled for several minutes, no ammonia is evolved, and on dilution and neutralisation with hydrochloric acid the unchanged nitrolamine separates.

Action of Nitrous Acid.—2·5 grams of the nitrolamine were dissolved in dilute hydrochloric acid and the temperature reduced below 5° by the addition of ice. One gram of sodium nitrite gradually added caused the liquid to become turbid with separation of a yellow oil, which on standing became resinous, whilst the solution developed a strong odour of carvone.

Hydrochloride.—On passing dry hydrogen chloride into cooled ether containing the nitrolamine in suspension, the hydrochloride separated almost immediately, and on crystallisation from alcohol fine, silky needles were deposited, which became discoloured at 220° and decomposed at 235—240°. The hydrochloride is also readily prepared by the addition of 15 per cent. hydrochloric acid to the nitrolamine, when it partially dissolves, and then sets to a hard cake of the hydrochloride:

0·3410 required 15·6 c.c. $N/10$ $AgNO_3$. Cl = 16·24.
0·3136 ,, 14·4 c.c. $N/10$ $AgNO_3$. Cl = 16·30.
$C_{11}H_{19}ON_2Cl$ requires Cl = 16·24 per cent.

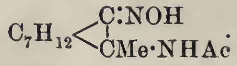
Platinichloride.—Concentrated aqueous solutions of the hydrochloride and platinic chloride were mixed together, when deep orange-coloured prisms slowly separated; these when crystallised from water decomposed at 185° with blackening and evolution of gas; the substance dissolves very readily in water or alcohol:

0·2206 gave 0·0556 Pt. Pt = 25·20.
$(C_{10}H_{18}ON_2)_2,H_2PtCl_6$ requires Pt = 25·2 per cent.

Oxalate.—This was prepared by addition of two molecular proportions of the nitrolamine to one of oxalic acid, each being dissolved in warm alcohol. A finely-divided, crystalline compound separated, which when filtered, washed several times with cold alcohol, and recrystallised from the hot dilute solvent, yielded flattened prisms melting at 235°. The oxalate is readily soluble in water, but only sparingly so in hot alcohol:

0·1488 gave 16·2 c.c. moist nitrogen at 20° and 765 mm. N = 12·53.
$(C_{10}H_{18}ON_2)_2,H_2C_2O_4$ requires N = 12·33 per cent.

Acetylpinene Nitrolamine,



$C_7H_{12}<\begin{array}{l}C{:}NOH\\ |\\ CMe\cdot NHAc\end{array}.$

Three grams of the nitrolamine were gradually added to 10 grams of acetic anhydride, solution took place with evolution of heat, and on heating the liquid on the water-bath it became light brown and somewhat viscous. On pouring into water an oil separated which was rendered crystalline by addition of ammonia; by recrystallisation from hot alcohol, the acetyl derivative was obtained in large, transparent, hexagonal prisms melting at 224° with decomposition:

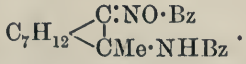
0·1418 gave 15·6 c.c. moist nitrogen at 20° and 765 mm. N = 12·65.

$C_{12}H_{20}O_2N_2$ requires N = 12·50 per cent.

The nitrolamine is soluble in dilute caustic soda, showing that the oximino-group has not been attacked; it also dissolves in dilute hydrochloric acid, being reprecipitated on addition of ammonia. Warm methyl or ethyl alcohol, acetic acid, or ethyl acetate dissolve the substance readily, chloroform, benzene, or ether more sparingly, whilst in light petroleum it is almost insoluble.

Sodium acetate and acetic anhydride were used in the hope of preparing the diacetyl compound, but only a black tar resulted, from which no crystallisable material could be obtained.

Dibenzoylpinene Nitrolamine,



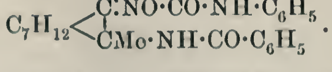
$C_7H_{12}<\begin{array}{l}C{:}NO\cdot Bz\\ |\\ CMe\cdot NHBz\end{array}.$

Five grams of the nitrolamine were dissolved in 10 per cent. aqueous caustic soda and treated with benzoyl chloride in the usual manner; an oil separated which soon solidified to a hard, compact mass. When ground with dilute aqueous caustic soda, filtered, washed, and recrystallised from alcohol, tufts of small, transparent prisms melting at 167° were deposited. The benzoyl derivative dissolves readily in warm methyl alcohol, acetic acid, benzene, or chloroform, crystallising from the solutions in bright but small, rhombic prisms. In ether it dissolves sparingly and is almost insoluble in light petroleum:

0·1718 gave 10·8 c.c. moist nitrogen at 15·5° and 762 mm. N = 7·36.

$C_{24}H_{36}O_3N_2$ requires N = 7·17 per cent.

The Diphenylcarbamide,



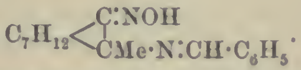
$C_7H_{12}<\begin{array}{l}C{:}NO\cdot CO\cdot NH\cdot C_6H_5\\ |\\ CMe\cdot NH\cdot CO\cdot C_6H_5\end{array}.$

Four grams of the dry nitrolamine were dissolved in 100 c.c. of warm, dry benzene and 5 grams of phenylcarbimide added; no immediate precipitation took place, but on cooling an oil separated, Addition of light petroleum caused the oil to solidify and precipitated from the benzene a finely-divided, crystalline powder. The crude product separates from most solvents as an oil, but on dissolving in alcohol and adding light petroleum, tufts of white, minute needles appear. These after two recrystallisations from hot alcohol yielded minute needles of the diphenylcarbamide melting at 133° with evolution of gas:

0·1264 gave 0·3178 CO_2 and 0·0806 H_2O. C = 68·57; H = 7·0.
0·1092 ,, 12·8 c.c. moist nitrogen at 19° and 777 mm. N = 13·75.
$C_{24}H_{28}O_3N_4$ requires C = 68·6; H = 6·7; N = 13·33 per cent.
$C_{17}H_{23}O_2N_3$,, C = 67·7; H = 7·6; N = 13·95 ,,

The pure compound is only sparingly soluble in cold solvents, but dissolves in hot methyl or ethyl alcohol, chloroform, or acetic acid. It is sparingly soluble in hot benzene and almost insoluble in light petroleum. As indicated by the analysis two molecular proportions of the carbimide combine with one of the nitrolamine.

Benzylidenepinene Nitrolamine,



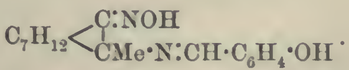
$C_7H_{12}{<}\begin{matrix}C{:}NOH\\ |\\ CMe{\cdot}N{:}CH{\cdot}C_6H_5\end{matrix}$.

Five grams of the nitrolamine were dissolved in 25 c.c. of absolute alcohol and 3 grams of benzaldehyde added, when the contents of the flask solidified to a hard, crystalline cake with considerable evolution of heat. The reaction was completed by heating the flask on the water-bath for three hours under a reflux condenser; on cooling, a compact mass of colourless, prismatic needles separated which, when filtered, washed with a little cold alcohol, and recrystallised twice from the hot solvent, furnished aggregates of prisms melting at 162°:

0·1424 gave 0·3924 CO_2 and 0·1088 H_2O. C = 75·15; H = 8·48.
0·1680 gave 15·4 c.c. moist nitrogen at 19° and 765 mm. N = 10·60.
$C_{17}H_{22}ON_2$ requires C = 75·55; H = 8·14 per cent.

The compound dissolves readily in warm alcohol, chloroform, benzene, or ether, crystallising in tufts of elongated prisms. It dissolves sparingly in cold light petroleum, but from the hot solution it is deposited as a bulky mass of fine needles. Aqueous caustic soda and dilute acids dissolve it sparingly, and on boiling with the latter, benzaldehyde is regenerated, whilst if ammonia is added to the solution the amino-oxime mixed with benzaldehyde is precipitated.

Salicylidenepinene Nitrolamine,



$C_7H_{12}{<}\begin{matrix}C{:}NOH\\ |\\ CMe{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH\end{matrix}$.

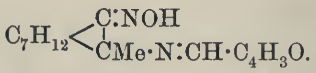
Three grams of the nitrolamine were dissolved in 15 c.c. of alcohol, and 2 grams of salicylaldehyde added; after heating on the water-bath a bright yellow colour was developed, and on pouring the solution into water a yellow oil was precipitated, which solidified in the course of twenty-four hours to a hard, crystalline mass. After being washed with cold alcohol and twice recrystallised from the hot solvent, bright, transparent sulphur-yellow prisms, melting sharply at 128°, were obtained:

0·1646 gave 14·4 c.c. moist nitrogen at 22° and 765 mm. $N = 9{\cdot}98$.

$C_{17}H_{22}O_2N_2$ requires $N = 9{\cdot}79$ per cent.

The substance dissolves readily in methyl or ethyl alcohols, giving pale yellow solutions, addition of ferric chloride producing a deep, purple-red coloration. Cold chloroform dissolves it readily, but the nitrolamine is precipitated from the solution by light petroleum in small clusters of bright yellow, four-sided prisms. It crystallises also from hot light petroleum in clusters of prisms, but dissolves to a greater extent in cold ether or acetic acid. Dilute caustic alkalis dissolve the substance readily, forming yellow solutions, from which it is precipitated by dilute hydrochloric acid, redissolving in excess of the acid.

Furfurylidene Pinene Nitrolamine,



$$C_7H_{12}<\begin{matrix}C{:}NOH\\ |\\ CMe{\cdot}N{:}CH{\cdot}C_4H_3O.\end{matrix}$$

Three grams of the nitrolamine were dissolved in 15 c.c. of absolute alcohol and 2 grams of furfuraldehyde added; condensation does not take place readily in the cold, but when heated for three hours the liquid became dark coloured, and when poured into water there was precipitated a brown, crystalline condensation product, which after three recrystallisations from hot alcohol became quite colourless, crystallising in small, well-defined cubes melting at 164° and remelting at the same temperature:

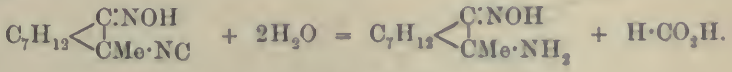
0·1262 gave 12·2 c.c. moist nitrogen at 22·5 and 764 mm. $N = 10{\cdot}97$.

$C_{15}H_{20}O_2N_2$ requires $N = 10{\cdot}76$ per cent.

The substance dissolves readily in hot methyl or ethyl alcohols, benzene, ether, or chloroform, being precipitated from the latter by light petroleum in clusters of prismatic needles; it dissolves sparingly in hot light petroleum, crystallising therefrom in needles.

Action of Chloroform and Caustic Potash.

Ten grams of the dry nitrolamine were dissolved in a mixture of 20 c.c. of absolute alcohol and 20 c.c. of chloroform; 15 grams of caustic potash dissolved in 40 c.c. of absolute alcohol and a little water were then added to the solution. Reaction took place in the cold with considerable development of heat, precipitation of a bulky mass of potassium chloride and production of a deep red colour in the solution. The liquid was then heated for half an hour on the water-bath, cooled, and filtered from the potassium chloride. It had the characteristically nauseous odour of an *iso*nitrile, and when rapidly evaporated gave a dark coloured oil, which decomposed on addition of water, yielding a dark coloured but crystalline mass of the nitrolamine. Potassium formate was recognised in the aqueous liquid after evaporation.



$$C_7H_{12}<\begin{array}{l}C{:}NOH\\ |\\ CMe\cdot NC\end{array} + 2H_2O = C_7H_{12}<\begin{array}{l}C{:}NOH\\ |\\ CMe\cdot NH_2\end{array} + H\cdot CO_2H.$$

Action of Reducing Agents.

(1) *Alkaline Reducing Agents.*—Ten grams of the nitrolamine were dissolved in 150 c.c. of amyl alcohol, heated to boiling, and 10 grams of sodium added gradually. The solution became yellow and small quantities of ammonia were liberated; on dilution with water and acidification with concentrated hydrochloric acid, the liquid separated into two layers, from which the amyl alcohol was removed by a current of steam. The acid liquid was then cooled and concentrated ammonia added, when a small quantity of oily liquid having an odour of cymene separated, together with a very bulky mass of the unchanged nitrolamine, which when dry weighed 9 grams. Similar results were obtained by the use of boiling ethyl alcohol and sodium.

(2) *Acid Reducing Agents.*—Dilute or glacial acetic acid and zinc dust left the nitrolamine unattacked, so that the action of alcoholic hydrochloric acid was tried. Twenty grams of the nitrolamine were added to a mixture of 50 c.c. of absolute alcohol and 150 c.c. of alcoholic hydrochloric acid; the solution became semi-solid owing to the separation of the hydrochloride. Twenty grams of zinc dust were then gradually added and the temperature kept below 50°. The solution soon became clear and, after standing for four hours, the acid was partially neutralised with caustic soda and the alcohol driven off with a current of steam. On evaporation, the distillate gave an oil having a strong odour of peppermint and weighing 3 grams. In order to prepare the oxime, the oil was dissolved in 10 c.c. of alcohol and heated with 2 grams of hydroxylamine hydrochloride and 0·6 gram of caustic potash in a reflux apparatus for several hours; on pouring the solution into water, an oil separated, which crystallised on addition of ice, and when recrystallised from alcohol the oxime melted at 86° (Wallach gives 86—87° for the oxime of pinocamphone). The liquid left in the distilling flask was made alkaline with caustic soda, when a strong basic odour was developed and ammonia was evolved. After passing steam through the liquid, a very small quantity of a basic oil

was obtained, but has not yet been identified; acidification of the liquid in the distilling flask and subsequent addition of ammonia gave a bulky, white precipitate of the unchanged nitrolamine which weighed nearly 12 grams.

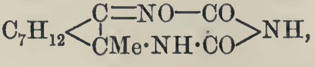
ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

II.—*A* pseudo-*Semicarbazide from Pinene.*

By FREDERICK PEACOCK LEACH.

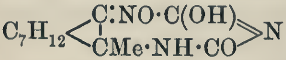
THE reaction between pinene nitrosochloride and potassium cyanate does not, as one might expect, lead to the production of a carbimide by the replacement of the chlorine by the $-N{:}C{:}O$ group, but instead gives rise to a somewhat complex ring compound having the empirical formula $C_{12}H_{17}O_3N_3$. Interaction between the nitrosochloride and potassium cyanate takes place quite readily in alcoholic solution at 45—50°, two molecular proportions of the cyanate reacting with one of the nitrosochloride.

The constitution of the new compound is probably best expressed by the formula



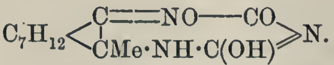
$$C_7H_{12}<\begin{matrix}C{=}NO{-}CO\\ |\\ CMe\cdot NH\cdot CO\end{matrix}>NH,$$

or one of the tautomeric forms,



$$C_7H_{12}<\begin{matrix}C{:}NO\cdot C(OH)\\ |\\ CMe\cdot NH\cdot CO\end{matrix}\geqslant N$$

and

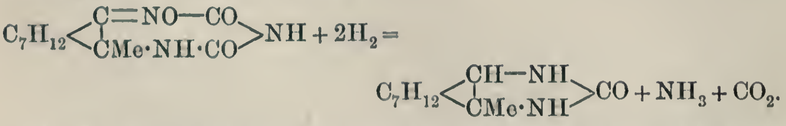


$$C_7H_{12}<\begin{matrix}C{=}NO{-}CO\\ |\\ CMe\cdot NH\cdot C(OH)\end{matrix}\geqslant N.$$

This conclusion has been reached by considering the following experimental evidence:

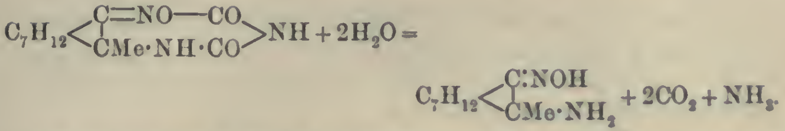
(1) The substance behaves like an imide, having a feebly acidic character, dissolving in caustic alkalis, and giving alkali salts like succinimide or phthalimide.

(2) When reduced by dilute acetic acid and zinc dust it loses carbon dioxide and ammonia, owing to liberation of cyanic acid, and a very stable *pseudo*carbamide is formed:



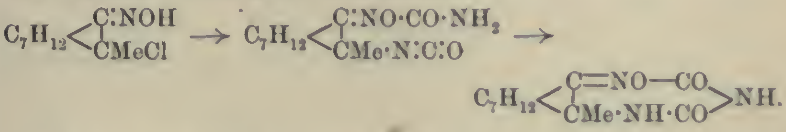
$$C_7H_{12}<\begin{matrix}C{=}NO{-}CO\\ |\\ CMe\cdot NH\cdot CO\end{matrix}>NH + 2H_2 = C_7H_{12}<\begin{matrix}CH{-}NH\\ |\\ CMe\cdot NH\end{matrix}>CO + NH_3 + CO_2.$$

(3) Warm concentrated sulphuric acid hydrolyses the imide and the ring undergoes disruption; carbon dioxide and ammonia are liberated and pinene nitrolamine is formed:



$$C_7H_{12}\Big<\begin{array}{l}C{=}NO{-}CO\\ CMe\cdot NH\cdot CO\end{array}\Big>NH + 2H_2O = C_7H_{12}\Big<\begin{array}{l}C{:}NOH\\ CMe\cdot NH_2\end{array} + 2CO_2 + NH_3.$$

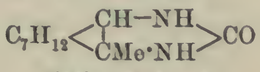
The mechanism by which the seven-membered ring is produced from the nitrosochloride has not been fully explained, but there seems no doubt that the condensation is brought about in some way by free cyanic acid, which can be recognised in the liquid by means of the cobalt acetate test. The most probable explanation depends on the resolution of the bimolecular nitrosochloride into the unimolecular (oximino) form, and replacement of the chlorine by the group $-N{:}C{:}O$; interaction of the free cyanic acid with the oximino-group would give a carbamic derivative of the oxime, which then undergoes rearrangement, forming the complex imide:



$$C_7H_{12}\Big<\begin{array}{l}C{:}NOH\\ CMeCl\end{array} \rightarrow C_7H_{12}\Big<\begin{array}{l}C{:}NO\cdot CO\cdot NH_2\\ CMe\cdot N{:}C{:}O\end{array} \rightarrow C_7H_{12}\Big<\begin{array}{l}C{=}NO{-}CO\\ CMe\cdot NH\cdot CO\end{array}\Big>NH.$$

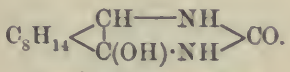
This new compound is exceedingly stable towards oxidising agents. Whilst pinene and its compounds are, generally speaking, readily oxidised or altogether destroyed by nitric acid, the new compound can be boiled with concentrated nitric acid (sp. gr. 1·42), and on dilution with water crystallises in needles. In a similar manner, when dissolved in cold alkali and treated with alkaline hypobromite, the unchanged substance is precipitated from the solution.

Towards reducing agents the substance is very sensitive, and as already pointed out it gives rise by the action of zinc and dilute acetic acid to a *pseudo*carbamide from which the corresponding nitroso-ψ-carbamide and *pseudo*semicarbazide have been obtained. These substances have a close relationship to the corresponding derivatives of camphor, recently isolated and examined by Forster and Fierz (Trans., 1905, 87, 110 and 722):



$$C_7H_{12}\Big<\begin{array}{l}CH{-}NH\\ CMe\cdot NH\end{array}\Big>CO$$

Pinyl-ψ-carbamide.



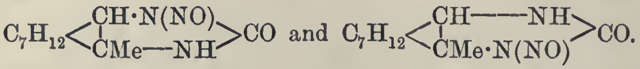
$$C_8H_{14}\Big<\begin{array}{l}CH{-}NH\\ C(OH)\cdot NH\end{array}\Big>CO.$$

Camphoryl-ψ-carbamide.

The *pseudo*carbamide from pinene possesses a very stable ring structure, for it sublimes unchanged at 224° and is scarcely acted on by hot 30 per cent. caustic potash or dilute acids. The camphoryl compound possesses a labile hydrogen atom, owing to which the ring can be opened by dilute acids, giving the carbamide of aminocamphor, from which alkalis regenerate the *pseudo*carbamide.

The action of nitrous acid on the *pseudo*carbamide from pinene gives rise to a nitroso-derivative, crystallising in beautiful yellow plates with a delicate pink lustre.

The stable nature of the ring in the *pseudo*carbamide makes it difficult to determine the position taken up by the nitroso-group: for the present, therefore, it is not possible to decide between the formulæ

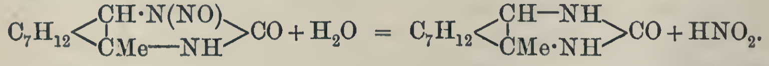


$$C_7H_{12}<\begin{array}{l}CH\cdot N(NO)\\ CMe—NH\end{array}>CO \text{ and } C_7H_{12}<\begin{array}{l}CH——NH\\ CMe\cdot N(NO)\end{array}>CO.$$

A similar uncertainty exists in the case of the *pseudo*semicarbazide.

Although remaining unchanged in the dark the nitroso-ψ-carbamide when exposed to light undergoes a series of interesting changes: in sunlight the colour changes in the course of a few minutes from the characteristic yellow with pink reflex to a bright green, whilst after some hours the green begins to fade and is followed by a dull yellow colour, further exposure causing no alteration; besides change of colour the crystals become opaque and "pitted" on the surface owing to escape of gas. This change, which is accompanied by decrease of fusibility, has been proved to be due to the elimination of the nitroso-group, with the regeneration of the *pseudo*carbamide. The readiness with which the nitroso-group is detached appears from the fact, that if a few crystals of the nitroso-compound are placed in a test-tube with a little potassium iodide and starch solution, and one drop of dilute sulphuric acid is added, the blue colour due to the liberation of iodine makes its appearance in the course of a few minutes.

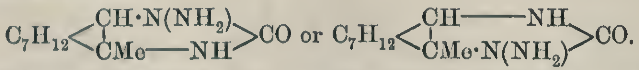
Cazeneuve (*Compt. rend.*, 1889, **109**, 185) noticed somewhat similar changes of colour in the case of nitrosocamphor (compare Claisen and Manasse, *Annalen*, 1893, **274**, 72):



$$C_7H_{12}<\begin{array}{l}CH\cdot N(NO)\\ CMe—NH\end{array}>CO+H_2O = C_7H_{12}<\begin{array}{l}CH—NH\\ CMe\cdot NH\end{array}>CO+HNO_2.$$

The introduction of the nitroso-group into the *pseudo*carbamide renders the product soluble in dilute caustic soda, from which the sodium salt is precipitated on further addition of cold concentrated caustic soda; if, however, the solution is heated, decomposition takes place, gas being evolved and an oil having a camphoraceous odour being produced. The products of the reaction are still under investigation.

The reduction of the nitroso-ψ-carbamide gives rise to a crystalline *pseudo*semicarbazide:

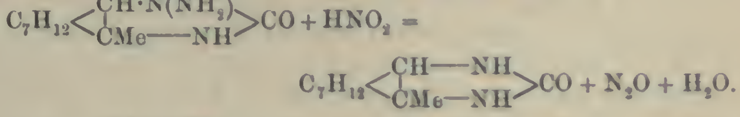


$$C_7H_{12}<\begin{array}{l}CH\cdot N(NH_2)\\ CMe——NH\end{array}>CO \text{ or } C_7H_{12}<\begin{array}{l}CH——NH\\ CMe\cdot N(NH_2)\end{array}>CO.$$

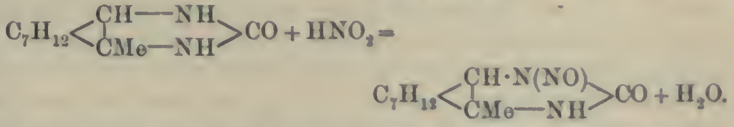
The tendency, however, for the nitroso-group to become eliminated as ammonia is very considerable, and unless the conditions given for the preparation of the *pseudo*semicarbazide are adhered to, a product is obtained which is very difficult to purify.

The new base resembles semicarbazide itself in combining with great readiness with aldehydes and ketones to form the corresponding *pseudo*-semicarbazones; with acetone, however, no condensation product has been obtained. The quinone-ψ-semicarbazone crystallises in bright yellow needles and contains one molecule of water of crystallisation, which it loses at 100°; products obtained by condensation of the *pseudo*semicarbazide with aldehydes, however, are free from solvent. The hydrochloride of the base when heated with nitrous acid at 0° regenerates the *pseudo*carbamide, and if excess of hydrochloric acid is present, the nitroso-ψ-carbamide is obtained, owing to the action of the nitrous acid on the *pseudo*carbamide.

The reaction is most probably expressed as follows:

(I) 

$$C_7H_{12}<\begin{matrix}CH\cdot N(NH_2)\\ CMe{-\!-}NH\end{matrix}>CO + HNO_2 = C_7H_{12}<\begin{matrix}CH{-\!-}NH\\ CMe{-\!-}NH\end{matrix}>CO + N_2O + H_2O.$$

(II) 

$$C_7H_{12}<\begin{matrix}CH{-\!-}NH\\ CMe{-\!-}NH\end{matrix}>CO + HNO_2 = C_7H_{12}<\begin{matrix}CH\cdot N(NO)\\ CMe{-\!-}NH\end{matrix}>CO + H_2O.$$

This observation is in agreement with that of Emil Fischer (*Annalen*, 1877, **190**, 158), who found that when sodium nitrite acted on phenylmethylhydrazine in dilute sulphuric acid the nitroso-compound of phenylmethylamine was obtained,

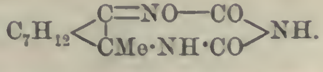
$$C_6H_5(CH_3)N\cdot NH_2 + 2HNO_2 = C_6H_5(CH_3)N\cdot NO + 2H_2O + N_2O,$$

this action doubtless also takes place in two stages.

The behaviour of the camphoryl-ψ-semicarbazide (Forster and Fierz, Trans., 1905, **87**, 826) resembles that of the pinene compound, if the reaction is carried out in acetic acid solution, when the *pseudo*-carbamide is obtained, but excess of sodium nitrite does not yield the nitroso-ψ-carbamide; it differs, however, in the fact that when the nitrate of the camphoryl-ψ-semicarbazide is treated with nitrous acid the ring undergoes disruption, with the formation of camphoryl azoimide.

The compounds of pinene described in this paper are optically inactive.

EXPERIMENTAL.

The Imide, 

$$C_7H_{12}<\begin{matrix}C{=}NO{-\!-}CO\\ CMe\cdot NH\cdot CO\end{matrix}>NH.$$

The most satisfactory method of obtaining this compound is to treat the nitrosochloride of pinene in quantities of 20 grams at a time, larger quantities cause the formation of more resinous matter. Twenty grams of freshly prepared pinene nitrosochloride were ground to a fine powder with 18 grams of potassium cyanate and the mixture added to 150 c.c. of rectified spirit, the whole being shaken from time to time. In the cold, the reaction proceeds very slowly, but on allowing to stand at 45—50° the nitrosochloride gradually disappeared and potassium chloride was precipitated along with a quantity of small, hard crystals of the imide, which is only very sparingly soluble in cold alcohol; the solution developed a pale yellow colour, owing to the formation of a certain amount of a yellow, resinous oil, and in about four days the whole of the nitrosochloride had disappeared; sufficient water was added to dissolve the potassium chloride and on filtering there was left an almost pure residue of the new compound, which after two recrystallisations from hot alcohol was quite pure. On pouring the alcoholic solution into a large volume of water a yellowish-white, bulky solid, mixed with small quantities of oily matter and regenerated pinene, was precipitated, from which after filtering, drying, and extracting, with light petroleum, the crude imide was obtained. The light petroleum, on evaporation, left a brown, resinous oil having an odour of turpentine, and after some time crystals were deposited, which when recrystallised twice from alcohol melted at 131° and gave no depression when mixed with nitrosopinene. From 100 grams of pinene nitrosochloride, 70 grams of the crude imide were obtained. The imide dissolves moderately in hot alcohol, crystallising in rosettes of hard prisms having the appearance of truncated octahedra, and after two recrystallisations the substance is quite colourless and melts at 238—240° with some previous discoloration. In cold solvents the new compound is only very sparingly soluble, but crystallises from hot, dilute acetic acid in prismatic needles, from hot methyl alcohol in small prisms, and from hot water, in which it is only slightly soluble, in needles; in basic solvents such as aniline or pyridine, the imide is readily soluble:

0·1139 gave 0·2388 CO_2 and 0·0704 H_2O. C = 57·18; H = 6·96.
0·1326 „ 0·2788 CO_2 „ 0·0843 H_2O. C = 57·34; H = 7·06.
0·1226 „ 18·2 c.c. moist nitrogen at 19° and 766 mm. N = 17·19.
$C_{12}H_{17}O_3N_3$ requires C = 57·37; H = 6·77; N = 16·73 per cent.
$C_{12}H_{18}O_3N_3$ „ C = 57·14; H = 7·14; N = 16·66 „ „

When boiled with dilute hydrochloric or sulphuric acid the substance is not changed and the solution when made alkaline does not reduce Fehling's solution; prolonged boiling, however, with concentrated hydrochloric acid decomposes it, giving oily products, and the solution yields a red precipitate of cuprous oxide on addition of Fehling's solution and caustic alkali.

Action of Nitric Acid.—The imide dissolves readily in cold concentrated nitric acid (sp. gr. 1·42), forming a colourless liquid with but slight development of heat; the liquid on boiling becomes yellow and a reaction appears to take place with evolution of red fumes: addition of water, however, precipitates the unchanged imide in fine needles. This behaviour is remarkable in a pinene derivative and supports the view that the substance is a ureide or ring compound of a very stable nature.

Potassium Salt.—2·5 grams of the imide were ground to a fine powder and mixed with 15 c.c. of cold alcohol, 0·6 gram of caustic potash dissolved in the smallest quantity of water was then added; the imide dissolved and almost immediately a solid, white mass of the potassium salt was precipitated, which, after filtering and washing with a little absolute alcohol, was dissolved in absolute alcohol and reprecipitated by addition of dry ether:

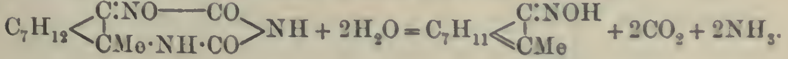
0·5855 gave 0·1737 K_2SO_4. K = 13·31.

$C_{12}H_{16}O_3N_3K$ requires K = 13·49 per cent.

The potassium salt is extremely soluble in cold water, and when carbon dioxide is passed into the solution the imide is precipitated as a very bulky mass of fine needles; exposure to air causes the salt to decompose slowly owing to the action of moisture and carbon dioxide. It dissolves readily in warm alcohol, from which it crystallises in large, rhombic prisms, but is insoluble in dry ether.

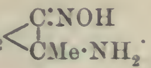
Sodium Salt.—This is prepared in a similar manner to the potassium salt; it differs, however, in being more soluble in cold alcohol. Addition of dry ether precipitates it in white and somewhat opaque needles.

Action of Alkali.—The imide dissolves very readily in dilute aqueous caustic alkalis, being reprecipitated by addition of dilute acids; if, however, the substance is boiled with 30 per cent. aqueous caustic potash, the liquid acquires a red colour and evolves ammonia. During the course of the reaction a crystalline deposit appeared in the condenser and proved to be nitrosopinene (m. p. 131°); after the evolution of ammonia had ceased the liquid was diluted with water and acidified with hydrochloric acid, when evolution of carbon dioxide and the separation of crystalline matter took place; the latter after recrystallisation yielded a considerable quantity of nitrosopinene:



$$C_7H_{12}\left\langle\begin{matrix}C{:}NO\text{——}CO\\ |\qquad\qquad\\ CMe\cdot NH\cdot CO\end{matrix}\right\rangle NH + 2H_2O = C_7H_{11}\left\langle\begin{matrix}C{:}NOH\\ |\\ CMe\end{matrix}\right. + 2CO_2 + 2NH_3.$$

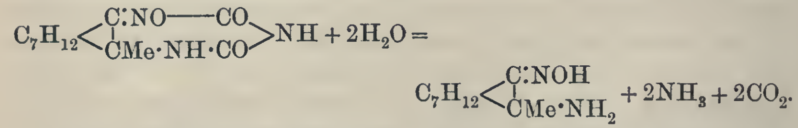
Conversion into Pinene Nitrolamine, $C_7H_{12}\left\langle\begin{matrix}C{:}NOH\\ |\\ CMe\cdot NH_2\end{matrix}\right.$.



Five grams of the imide were added gradually to 20 c.c. of concentrated sulphuric acid, when considerable development of heat occurred, and a colourless solution was formed; on heating to 85°, effervescence took place with evolution of carbon dioxide and formation of ammonium sulphate, the liquid became pale yellow and finally red. After the evolution of gas had ceased, the liquid was cooled and poured on to crushed ice, yielding a clear solution. Addition of aqueous caustic soda gave a crystalline precipitate which immediately dissolved in excess of the alkali, and the colour of the solution changed from red to yellow; carbon dioxide changed the colour to red again and precipitated a crystalline deposit of fine needles, which, when filtered and recrystallised from alcohol, softened at 118° and melted at 123° with evolution of gas. Further recrystallisation did not alter the melting point, and the substance remelted at 129—131°, behaving exactly like pinene nitrolamine:

0·1800 gave 24·0 c.c. moist nitrogen at 20° and 772 mm. N = 15.50.
$C_{10}H_{18}ON_2$ requires N = 15·38 per cent.

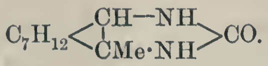
When mixed with pinene nitrolamine, obtained by the action of ammonia on pinene nitrosochloride (see preceding paper, page 4), no depression of the melting point took place. It forms a hydrochloride identical with that of pinene nitrolamine, and therefore its identity is established:



$$C_7H_{12}<\begin{matrix}C{:}NO\text{——}CO \\ |\quad\quad\quad\quad \\ CMe{\cdot}NH{\cdot}CO\end{matrix}>NH + 2H_2O = C_7H_{12}<\begin{matrix}C{:}NOH \\ | \\ CMe{\cdot}NH_2\end{matrix} + 2NH_3 + 2CO_2.$$

In order to ascertain whether free nitrogen was eliminated during the reaction between the sulphuric acid and imide, a weighed quantity of the latter was placed in a small flask attached to a carbon dioxide apparatus and a nitrometer in the usual manner, when it was found that the whole of the gas expelled on warming the flask to 100° was absorbed by the caustic potash in the nitrometer, and on adding caustic potash to the diluted sulphuric acid solution in the flask, ammonia was evolved.

Pinyl-ψ-carbamide,



$$C_7H_{12}<\begin{matrix}CH\text{—}NH \\ | \\ CMe{\cdot}NH\end{matrix}>CO.$$

Twenty grams of the imide were powdered and suspended in a mixture of 75 c.c. of glacial acetic acid and 40 c.c. of water, 35 grams of zinc dust were gradually added to the pasty liquid, and the mixture shaken from time to time, the temperature not being allowed to rise above 50°. In a short time the liquid became frothy, owing to the evolution of carbon dioxide, and had an odour recalling that of an *iso*cyanate. The elimination of ammonia took place simultaneously, and was detected by addition of caustic alkali to a small portion of the solution. When the liquid had become quite clear, it was heated on the water-bath for an hour, and on adding ammonia, a bulky, white precipitate of small needles, mixed with some oily matter, was obtained, which when filtered and dried gave a pale brown product with an odour of peppermint, due no doubt to the formation of small quantities of the ketone (Wallach's pinocamphone).

From 100 grams of the imide, 60 grams of the crude, dry pinyl-ψ-carbamide were obtained, giving, after recrystallisation from hot dilute alcohol, aggregates of colourless but almost opaque prismatic needles melting at 224° without decomposition. The crystals when deposited from the solution were transparent, but after separating and drying in the desiccator became opaque, probably due to loss of solvent of crystallisation:

0·1121 gave 0·2782 CO_2 and 0·0940 H_2O. C = 67·67; H = 9·31.

0·1798 ,, 22·6 c.c. moist nitrogen at 17° and 758 mm. N = 14·61.

$C_{11}H_{18}ON_2$ requires C = 68·04; H = 9·26; N = 14 43 per cent.

The *pseudo*carbamide is readily soluble in hot water, methyl alcohol or acetic acid, sparingly so in chloroform or ether, whilst in light petroleum it is almost insoluble. Cold concentrated sulphuric acid dissolves the *pseudo*carbamide, which is reprecipitated by ammonia. When heated with 30 per cent. aqueous caustic potash no ammonia was evolved, the substance appearing quite unchanged. The very stable nature of the *pseudo*carbamide is further emphasised by the fact that, when heated in a dry test-tube, it sublimes and condenses in small leaflets on the sides of the tube.

Reduction of the Imide by Glacial Acetic Acid and Zinc.

In the first experiments on the reduction of the imide it was noticed that if glacial acetic acid and zinc dust were used, a white, crystalline, but very insoluble compound separated from the liquid, and although a certain amount of the *pseudo*carbamide was produced, it was largely contaminated with this insoluble substance. Thirty grams of the imide were suspended in 200 c.c. of glacial acetic acid and 40 grams of zinc dust gradually added with shaking; after a short time an almost clear solution resulted, and the reaction was completed by heating for several hours on the water-bath. Water was then added to dissolve zinc acetate, and the liquid on being decanted from the zinc residues contained the insoluble matter in suspension; after filtration and washing with water, a colourless, crystalline compound was left which was insoluble in boiling alcohol or other solvents, except hot acetic acid, from which it crystallised on cooling in small, hard prisms which did not melt below 300°.

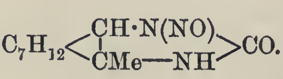
The filtered liquid when poured into water gave a further quantity of the insoluble substance, and after filtration and addition of ammonia a crystalline deposit of the *pseudo*carbamide was obtained:

0·1282 gave 0·3000 CO_2 and 0·1026 H_2O. $C = 63·82$; $H = 8·89$.
0·1418 ,, 15·7 c.c. moist nitrogen at 19° and 753 mm. $N = 12·59$.
$C_{12}H_{20}O_2N_2$ requires $C = 64·28$; $H = 8·92$; $N = 12·50$ per cent.

When this substance was heated in the water-oven, acetic acid was given off, and after being dried at 100° it lost 10 per cent. of its weight; the whole of the acetic acid, however, was not evolved, because on warming a small portion of the dried substance in a test-tube the pungent and characteristic odour was noticed.

This compound is insoluble in dilute acids and alkalis, but dissolves in concentrated sulphuric or nitric acid, and on dilution is precipitated unchanged. Reduction of the imide by alcoholic hydrochloric acid and zinc dust also yielded small quantities of the same insoluble compound, and it is hoped that further investigation will elucidate its constitution.

Pinylnitroso-ψ-carbamide,



$$C_7H_{12}<\begin{matrix}CH\cdot N(NO)\\ |\\ CMe\text{---}NH\end{matrix}>CO.$$

Twenty grams of the *pseudo*carbamide were made into a paste with water and mixed with 200 c.c. of water and 20 c.c. of concentrated hydrochloric acid, the liquid was cooled to 0° by the addition of crushed ice, and 10 grams of sodium nitrite added in small portions at a time with stirring. The *pseudo*carbamide was rapidly attacked, and a pale yellow, bulky solid was precipitated; after standing for an hour the liquid was filtered, when 19 grams of a bright sulphur-yellow nitroso-compound were obtained which crystallised from alcohol in small, yellow, hexagonal plates with a distinct red lustre when viewed by reflected light:

0·1127 gave 0·2436 CO_2 and 0·0798 H_2O. $C = 58·95$; $H = 7·86$.
0·1072 ,, 17·4 c.c. moist nitrogen at 17° and 754 mm. $N = 18·68$.
$C_{11}H_{17}O_2N_8$ requires $C = 59·19$; $H = 7·62$; $N = 18·83$ per cent.

The nitroso-ψ-carbamide gives the Liebermann reaction in all its stages, but so far its action towards aniline has not been studied; it is readily soluble in methyl or ethyl alcohol, from which it crystallises in plates; it dissolves in chloroform or acetic acid, being precipitated from the former by light petroleum in clusters of needles; in warm benzene it is only moderately soluble, and very sparingly so in light petroleum.

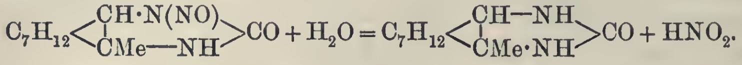
Action of Caustic Alkali.—The nitroso-ψ-carbamide dissolves in 10 per cent. alkali, giving a colourless solution, and on addition of a concentrated solution of the alkali the sodium salt is precipitated in pearly leaves, which, after filtration, washing with a little alcohol, and drying on a porous plate, yield a colourless but impure substance. If, however, the nitroso-compound is warmed with 25 per cent. aqueous caustic soda it partially dissolves, and on further warming a yellow oil appears with evolution of gas; the liquid has a camphoraceous odour, and on cooling yields a semi-solid, crystalline mass; addition of dilute sulphuric acid with a few drops of starch and potassium iodide solution gives an intense blue colour, showing that nitrous acid has been withdrawn from the nitroso-ψ-carbamide. The investigation of the products of the reaction is not yet complete.

Action of Light on the Nitroso-ψ-carbamide.

When freshly prepared the nitroso-compound is yellow with a delicate pink reflex; it was noticed, however, that if left exposed to light and air the crystals soon developed a bright green colour. Some experiments were therefore made in order to ascertain to what cause this change of colour is due. When the nitroso-ψ-carbamide is spread out in a thin layer on a flat-bottomed dish, covered with a clock glass, and exposed to sunlight, the colour of the crystals changes in the course of a few minutes to a bright, opalescent green and after some time to a deeper tint; examined by the lens, the surface of the crystals appears quite bright and the colouring uniform, but after exposure for some hours the green tint begins to fade and the surface becomes white and opaque. The crystals lose their transparent character and finally, after about a week's exposure, they become dull yellow, further exposure causing no alteration.

The melting point of the pure nitroso-ψ-carbamide is 161°, but after exposure the crystals did not melt until 190° was reached, and then after considerable previous softening. On examination under the microscope, the crystals were no longer bright and transparent, but of a dull uniform yellow colour, the surface of the crystals appearing "pitted" as if gas had escaped and minute crystals had grown on the surface of the larger ones, whilst the angles had lost their sharp and well-defined character. The product obtained after exposure differed from the nitroso-ψ-carbamide in being insoluble in dilute caustic alkalis and in not giving the Liebermann reaction; after recrystallisation from dilute alcohol the melting point gradually rose to 222°, and on mixing with the pinyl-ψ-carbamide no depression was observed. In order to prove its identity with the latter substance, a small quantity of the recrystallised product was added to crushed ice mixed with a little dilute hydrochloric acid; addition of sodium nitrite precipitated the original nitroso-ψ-carbamide melting at 161°.

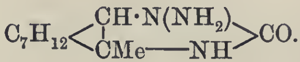
The fact, therefore, that the nitroso-ψ-carbamide eliminates the nitroso-group when exposed to light is proved; it appears probable, however, that this change is brought about by the action of moisture, causing hydrolysis:



$$C_7H_{12}{<}\begin{array}{l}CH\cdot N(NO)\\ CMe\text{—}NH\end{array}{>}CO + H_2O = C_7H_{12}{<}\begin{array}{l}CH\text{—}NH\\ CMe\cdot NH\end{array}{>}CO + HNO_2.$$

This hypothesis was tested by placing a small quantity of the nitroso-compound in a test-tube with two or three c.c. of distilled water, and a few drops of potassium iodide and starch solution, but no colour appeared after several hours; on repeating the experiment with the addition of one drop of dilute sulphuric acid, the blue colour appeared in a few minutes.

Pinyl-ψ-semicarbazide, $C_7H_{12}{<}\begin{array}{l}CH\cdot N(NH_2)\\ CMe\text{——}NH\end{array}{>}CO.$



Twenty grams of the nitroso-ψ-carbamide were made into a paste with 20 c.c. of water, and mixed with 150 c.c. of water and sufficient crushed ice to reduce the temperature below 5°. Twenty-five c.c. of glacial acetic acid were added, and 25 grams of zinc dust stirred in gradually, together with more ice if necessary. The yellow nitroso-compound dissolved slowly, forming a clear solution, and after half-an-hour had elapsed 10 c.c. of acetic acid were added, the reduction being complete in about two hours. The liquid was then filtered from zinc and evaporated to 500 c.c. The acetic acid, after being partially neutralised by addition of concentrated ammonia, caused the precipitation of brown, viscid matter, and after filtration a nearly colourless liquid was obtained, from which by further addition of ammonia the *pseudo*semicarbazide was precipitated in a fairly pure condition. From 20 grams of the nitroso-ψ-carbamide, 9 grams of the *pseudo*semicarbazide were obtained, which crystallised from hot alcohol in colourless, small, rhombic prisms melting at 209°. The specimen analysed was dried at 100° for half-an-hour:

0·1360 gave 0·3138 CO_2 and 0·1158 H_2O. $C = 62·92$; $H = 9·46$.
0·1074 „ 19·2 c.c. moist nitrogen at 19° and 752 mm. $N = 20·32$.
$C_{11}H_{19}ON_3$ requires $C = 63·15$; $H = 9·09$; $N = 20·09$ per cent.

The *pseudo*semicarbazide dissolves readily in warm methyl or ethyl alcohol, chloroform, or acetic acid, and moderately in warm acetone or benzene, crystallising from the latter in transparent plates; it is sparingly soluble in ether, and insoluble in light petroleum, and crystallises from water in tufts of minute needles. Towards ammoniacal silver nitrate it acts as a powerful reducing agent, giving a black deposit of metallic silver in the cold; with Fehling's solution, however, no action takes place, but on warming a copious precipitate of cuprous oxide is deposited, evolution of gas occurs, and an oil separates, having at first an odour of peppermint (probably pinocamphone) and, after the lapse of a few minutes, distinctly that of carvone. This reaction appears to be similar to that observed by Forster and Fierz (Trans., 1905, **87**, 727), who found that oxidation of camphoryl-ψ-semicarbazide with Fehling's solution gave rise to camphor.

Ferric chloride added to a cold alcoholic solution of the ψ-semicarbazide caused a slight evolution of gas which became much more brisk on warming; addition of water precipitated a white, crystalline substance.

The *pseudo*semicarbazide did not give a platinichloride, for on warming the solution became dark, evolved gas, and yielded a tarry residue with an odour of turpentine; in this respect the *pseudo*semicarbazide of pinene behaves like semicarbazide itself (Thiele and Stange, *Annalen*, 1894, **283**, 21).

The *hydrochloride* was obtained by passing dry hydrogen chloride into a solution of the *pseudo*semicarbazide in ether, a finely-divided, crystalline precipitate separated, and when filtered and recrystallised from absolute alcohol was deposited in thin, lustrous plates decomposing indefinitely at 250°:

0·3978 dissolved in water required 16·4 c.c. $N/10$ $AgNO_3$. Cl = 14·58.

$C_{11}H_{20}ON_3Cl$ requires Cl = 14·45 per cent.

No indicator need be used in the titration because the slightest excess of silver is shown by the solution turning black, owing to the strong reducing action of the *pseudo*semicarbazide. Towards hot concentrated hydrochloric acid the base is quite stable, the hydrochloride being deposited on cooling.

Copper Nitrate Double Salt.—The base, dissolved in the least quantity of dilute nitric acid, was added to a concentrated solution of copper nitrate in absolute alcohol; from the green solution bright blue needles were deposited, and after recrystallisation from hot water the *cuprinitrate* was obtained in tufts of blue needles decomposing about 175°:

0·1760 gave 0·0194 CuO. Cu = 8·79.

$(C_{11}H_{19}ON_3,HNO_3)_2,Cu(NO_3)_2$ requires Cu = 8·68 per cent.

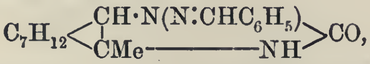
The Pinyl-ψ-semicarbazones.

Pinyl-ψ-semicarbazide combines with aldehydes and ketones with great readiness; with acetone, however, no condensation product has been obtained.

The base is dissolved in dilute acetic acid, diluted largely with water and the requisite quantity of the aldehyde or ketone, also dissolved in dilute acetic acid, added. The liquid becomes turbid, and on gently warming the *pseudo*semicarbazone separates, often as a viscid oil, soon becoming crystalline, or directly in a crystalline condition.

With the exception of the quinone-ψ-semicarbazone, there appears to be little or no tendency to combine with the solvent such as was exhibited in the case of the corresponding camphoryl derivatives (Forster and Fierz, Trans., 1905, **87**, 725); the quinone compound, however, retains one molecule of water, which is not lost in the desiccator, but on heating to 100° is completely eliminated.

Benzylidene Pinyl-ψ-semicarbazone,



$$C_7H_{12}<\begin{matrix}CH\cdot N(N\colon CHC_6H_5) \\ CMe\text{————}NH\end{matrix}>CO,$$

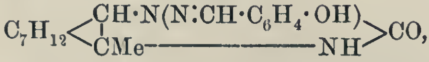
is precipitated by the addition of benzaldehyde to the solution of the base in dilute acetic acid. It crystallises from alcohol in rhombic prisms which melt at 180°, remelting at the same temperature. It dissolves readily in cold chloroform, and is reprecipitated by light petroleum in colourless, rhombic prisms; it dissolves readily in cold acetic acid, but is much less soluble in ether and almost insoluble in light petroleum:

0·1491 gave 18·4 c.c. moist nitrogen at 18° and 770 mm. N = 14·45.

$C_{18}H_{23}ON_3$ requires N = 14·14 per cent.

The benzylidene derivative is insoluble in dilute hydrochloric acid, but when heated hydrolysis takes place, giving a strong odour of benzaldehyde.

Salicylidene Pinyl-ψ-semicarbazone,



$$C_7H_{12}<\begin{matrix}CH\cdot N(N\colon CH\cdot C_6H_4\cdot OH) \\ CMe\text{————}NH\end{matrix}>CO,$$

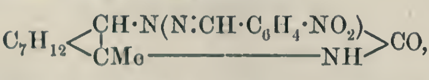
when crystallised from hot alcohol, in which it is only moderately soluble, yields small, hard, rhombic prisms melting at 252°. It is moderately soluble in chloroform, methyl alcohol, or acetic acid, sparingly so in warm benzene and insoluble in light petroleum:

0·1522 gave 17·6 c.c. moist nitrogen at 18° and 770 mm. N = 13·54.

$C_{18}H_{23}O_2N_3$ requires N = 13·41 per cent.

The salicylidene derivative dissolves in dilute aqueous caustic potash, and is reprecipitated on addition of dilute hydrochloric acid. The alcoholic solution with ferric chloride gives an intense green coloration, which is not altered by dilute hydrochloric acid.

m-*Nitrobenzylidene Pinyl-ψ-semicarbazone,*



$$C_7H_{12}<\begin{matrix}CH\cdot N(N\colon CH\cdot C_6H_4\cdot NO_2) \\ CMe\text{————}NH\end{matrix}>CO,$$

separated from the solution as a yellow, viscid solid, which soon hardened and crystallised. It dissolves sparingly in nearly all solvents, forming yellowish-green solutions; from hot alcohol it crystallises in pale yellow, small, hard prisms melting at 216°. On cooling, it solidifies to a clear, glassy mass, then crystallises, and on reheating melts at a lower temperature:

0·1056 gave 15 c.c. moist nitrogen at 17·5° and 765 mm. N = 16·54.
$C_{18}H_{22}O_3N_4$ requires N = 16·37 per cent.

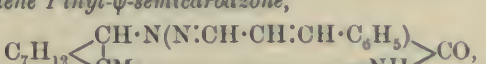
p-*Methoxybenzylidene Pinyl-ψ-semicarbazone*,

$$C_7H_{12}<\begin{matrix}CH\cdot N(N{:}CH\cdot C_6H_4\cdot OCH_3)\\ CMe\text{————————}NH\end{matrix}>CO,$$

separates from hot alcohol in transparent and well-defined rhombic prisms melting at 224—225°, and remelts at the same temperature. It dissolves readily in warm alcohol, chloroform, or acetic acid, and is sparingly soluble in warm ether or light petroleum, crystallising from the latter in small clusters of prisms; from dilute acetic acid clear flat prisms were deposited, but the odour of the aldehyde was distinctly noticeable in the liquid, owing no doubt to a partial hydrolysis:

0·1622 gave 18·7 c.c. moist nitrogen at 23° and 771 mm. N = 13·16.
$C_{19}H_{27}O_2N_3$ requires N = 12·79 per cent.

Cinnamylidene Pinyl-ψ-semicarbazone,

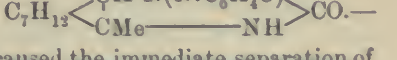


$$C_7H_{12}<\begin{matrix}CH\cdot N(N{:}CH\cdot CH{:}CH\cdot C_6H_5)\\ CMe\text{————————}NH\end{matrix}>CO,$$

crystallises from hot alcohol in small, colourless prisms melting at 236° with slight discoloration. It dissolves sparingly in cold methyl or ethyl alcohols, but readily in the warm solvents, and crystallises from the former in transparent, four-sided prisms; it is soluble in chloroform or warm benzene, but sparingly so in ether or light petroleum:

0·1504 gave 17·2 c.c. moist nitrogen at 21° and 766 mm. N = 13·12.
$C_{20}H_{25}ON_3$ requires N = 13·00 per cent.

Quinone Pinyl-ψ-semicarbazone,



$$C_7H_{12}<\begin{matrix}CH\cdot N(N{:}C_6H_4O)\\ CMe\text{————}NH\end{matrix}>CO.—$$

Addition of the quinone to the base caused the immediate separation of a bulky, brown crystalline precipitate from the deep red solution. When crystallised from alcohol, dark yellow needles are formed, which decompose at 194° with evolution of gas. The substance dissolves readily in chloroform, methyl or ethyl alcohol, or acetone, giving deep orange-coloured solutions; it is sparingly soluble in ether or light petroleum, giving bright yellow solutions; it dissolves also in warm dilute caustic potash to an orange-coloured solution, and on addition of dilute hydrochloric acid a deep green precipitate is obtained. When heated to 100°, the colour changes from yellow to orange, and the compound loses weight corresponding to one molecule of water; two separately prepared specimens were analysed:

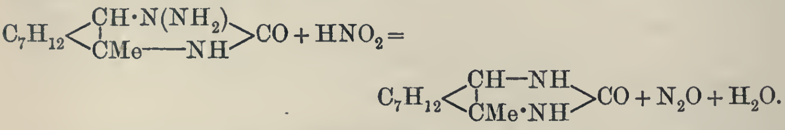
0·1644 gave 19·2 c.c. moist nitrogen at 22° and 770 mm. N = 13·40.
0·1480 „ 17·3 c.c. „ 19° „ 766 „ N = 13·54.
0·2126 lost 0·0118 at 100°; $H_2O = 5·55$.

$C_{17}H_{21}O_2N_3$ requires N = 14·04 per cent.
$C_{17}H_{21}O_2N_3,H_2O$ „ N = 13·24; $H_2O = 5·67$ per cent.

Acetone Pinyl-ψ-semicarbazone.—Addition of acetone to the dilute acetic acid solution of the base gave no precipitate on warming; in dilute ammoniacal solution an oil separated, from which, on standing, the *pseudo*semicarbazide crystallised.

Action of Nitrous Acid on the Hydrochloride of the pseudo-*Semicarbazide.*

The hydrochloride was dissolved in water and cooled to 0° by the addition of ice, and exactly one molecular proportion of sodium nitrite was added. The liquid became turbid, and a white, crystalline precipitate of the *pseudo*carbamide separated:



$$C_7H_{12}<\begin{matrix}CH\cdot N(NH_2)\\ | \\ CMe\text{——}NH\end{matrix}>CO + HNO_2 = C_7H_{12}<\begin{matrix}CH\text{—}NH\\ | \\ CMe\cdot NH\end{matrix}>CO + N_2O + H_2O.$$

The presence of the nitrous oxide was not proved. When the *pseudo*semicarbazide was dissolved in dilute nitric or hydrochloric acid and sodium nitrite added, a white precipitate separated at first, and soon afterwards a yellow oil which crystallised, and on examination proved to be the nitroso-ψ-carbamide melting at 161°.

Royal College of Science, London,
South Kensington, S.W.

III.—*The Liquid Volume of a Dissolved Substance.*

By John Scott Lumsden.

The following investigation was undertaken in order to obtain some information regarding the volume assumed by a solid, liquid, or gas when dissolved in a liquid on which it exerts no chemical action.

It is well known that the values determined for atomic volumes and atomic refractions from experiments made on pure liquids hold with fair accuracy when applied to solids and liquids in solution; and the inference is, that a liquid retains its own volume when dissolved and that a solid assumes in solution the volume which the same weight would have if it existed as a liquid at the same temperature.

If that inference is correct, or if it can be proved to vary from exactness in a rational manner, a law of the liquid volume of a dissolved substance is revealed and the experimental results here recorded show that there is such a law, which holds, not only for the volume assumed by a solid or liquid, but also for the volume taken by a dissolved gas.

At the beginning of the investigation it was found necessary to exclude from consideration solutions in which water was the solvent, since solution in water is of the nature of combination and is always accompanied by a marked shrinking in volume; a further contraction also occurs if the dissolved substance becomes ionised.

The first experiments were designed to prove that a dissolved substance behaves as a liquid and does not undergo any sudden change in volume as the temperature is raised above its normal melting point or boiling point. A number of substances of widely different composition were chosen; these were dissolved in various solvents and the volume of the molecular weight in grams of each substance was measured at several temperatures. A quantity of substance was weighed in a short-necked, stoppered flask, the solvent was added and the flask was reweighed. A pyknometer was filled with the solution obtained in this way by inserting the point of the instrument into the flask and withdrawing the liquid, and a similar pyknometer was filled with the solvent. The pyknometers were then placed together in a thermostat and after remaining a sufficient time at the desired temperature they were removed, dried, and weighed. The capacity of each pyknometer was carefully determined at several temperatures and by interpolation the capacity at any desired temperature was obtained. All the weighings were corrected to the weight in a vacuum and the densities are referred to water at 4°, thus making the number which expresses the molecular volume represent also the volume in cubic centimetres of the molecular weight in grams of the substance at the temperature given.

The molecular volume in solution was calculated by the usual formula: $Vm = \frac{M + s}{D} - \frac{s}{d}$, where M is the molecular weight of the substance, D the density of the solution, d the density of the solvent, and s the weight of the solvent used to dissolve the molecular weight in grams of the substance.

Molecular Volume of Naphthalene in Toluene.

2·7933 grams of naphthalene were dissolved in 19·7216 grams of toluene:

Temp.	Sp. gr. toluene.	Sp. gr. solution.	Vol. of 128 g. naphthalene. In solution.	Vol. of 128 g. naphthalene. As liquid.
15°	0·8706	0·8885	123·28	—
25	0·8612	0·8791	124·25	—
40	0·8476	0·8653	126·05	(79·9°)
60	0·8296	0·8473	128·42	130·92 *
80	0·8113	0 8287	131·05	(98·4°)
100	0·7931	0·8104	133·64	133·04 †

* Schiff, *Annalen*, 1884, **223**, 261.
† Nasini, *Gazzetta*, 1885, **15**, 84.

Molecular Volume of Phenylacetic Acid in Toluene.

3·1889 grams of acid were dissolved in 19·6646 grams of toluene:

Temp.	Sp. gr. toluene.	Sp. gr. solution.	Vol. of 136·08 g. acid. In solution.	Vol. of 136·08 g. acid. As liquid.
15°	0·8706	0·8998	119·91	*
25	0·8612	0·8906	120·60	
40	0·8476	0·8770	122·04	(76·6°) 125·50
60	0·8296	0·8590	123·84	(86·2°)
80	0·8113	0·8405	125·88	126·41
100	0·7931	0·8223	127·90	(89·5°) 126·73

* Schiff, *Annalen*, 1884, **223**, 260.

Molecular Volume of Thymol in Benzene.

2·0108 grams of thymol were dissolved in 14·1864 grams of benzene:

Temp.	Sp. gr. benzene.	Sp. gr. solution.	Vol. of 150 g. thymol. In solution.	Vol. of 150 g. thymol. As liquid.
15°	0·8846	0·8943	154·74	*
25	0·8742	0·8842	156·01	
35	0·8639	0·8740	157·50	(49·3°) 157·91
45	0·8536	0·8638	158·99	(58·3°)
55	0·8432	0·8535	160·58	159·08 (64°)
65	0·8328	0·8432	162·26	159·78

* Schiff, *Annalen*, 1884, **223**, 259.

Molecular Volume of Dichlorobenzene in Carbon Tetrachloride.

2·0677 grams were dissolved in 30·3615 grams of carbon tetrachloride :

			Vol. of 146·9 g. dichlorobenzene.	
Temp.	Sp. gr. CCl_4.	Sp. gr. solution.	In solution.	As liquid.
15°	1·6039	1·5794	113·93	—
25	1·5845	1·5608	114·77	—
35	1·5652	1·5425	115·48	*
45	1·5462	1·5244	116·33	(53°)
55	1·5275	1·5065	117·18	117·53
65	1·5075	1·4876	117·95	(63°) 118·36

* Schiff, *Annalen*, 1884, **223**, 263.

Molecular Volume of o-*Nitrophenol in Chloroform.*

1·1628 grams of nitrophenol were dissolved in 12·9120 grams of chloroform :

			Vol. of 139 g. nitrophenol.	
Temp.	Sp. gr. $CHCl_3$.	Sp. gr. solution.	In solution.	As liquid.
15°	1·4898	1·4774	102·80	*
25	1·4721	1·4605	103·56	(35°) 106·48
35	1·4531	1·4423	104·31	(45·2°)
45	1·4344	1·4247	105·06	107·38
55	1·4163	1·4071	105·91	(55°) 108·29

* Schiff, *Annalen*, 1884, **223**, 263.

Molecular Volume of Chloroform in Toluene :

			Vol. of 119·4 g. chloroform.	
Temp.	Sp. gr. toluene.	Sp. gr. solution.	In solution.	As liquid.
40°	0·8472	0·9647	82·98	(20°) 80·21 *
60	0·8290	0·9427	85·39	(40) 83·33
80	0·8105	0·9203	88·02	(60) 84·62

* Thorpe, Trans., 1880, **37**, 196.

Molecular Volume of Bromine in Carbon Tetrachloride.

3·4716 grams of bromine were dissolved in 28·3596 grams of CCl_4 :

			Vol. of 79·96 g. bromine.	
Temp.	Sp. gr. CCl_4.	Sp. gr. solution.	In solution.	As liquid.
40°	1·5555	1·6379	27·70	26·22 *
50	1·5362	1·6178	27·98	26·52
60	1·5173	1·5981	28·27	26·83
70	1·4969	1·5769	28·57	—
75	1·4892	1·5687	28·74	—

* Thorpe, Trans., 1880, **37**, 174.

Molecular Volume of Naphthalene in Quinoline:

Temp.	Sp. gr. quinoline.	Sp. gr. solution.	Vol. of 128 g. naphthalene. In solution.	Vol. of 128 g. naphthalene. As liquid.
15°	1·0978	1·0887	123·73	
40	1·0785	1·0691	126·40	(79°)* 130·34
80	1·0478	1·0378	130·85	(130·7°) 136·78
120	1·0150	1·0057	134·61	(173·8°) 141·99
160	0·9826	0·9735	139·20	(193·6°) 143·37
200	0·9489	0·9394	144·93	(217°) 147·57
220	0·9319	0·9234	146·56	

* Lossen and Zander, *Annalen*, 1884, **225**, 111.

These molecular volumes are represented by curves on the accompanying diagram and the continuity of the curves makes it apparent that with rise of temperature the increase of volume is regular and that no breaks occur at the normal melting points or boiling points of the dissolved substances. Liquids, such as bromine and chloroform, when in solution were raised to temperatures above their boiling points, but their volumes did not undergo any sudden change; similarly, solids such as naphthalene and thymol when in solution were raised to temperatures above their melting points, but their curves of volume are continuous; and in the example given of a solution of naphthalene in quinoline, the change of temperature includes the regions at which the naphthalene normally exists as solid, liquid, and gas, yet there are no breaks in the curve of volume. In solution there is, therefore, only one phase, namely, the liquid phase, and a substance in solution at any temperature behaves as a simple liquid.

The next point on which information was sought was the relation between the volume of a pure liquid and its volume when dissolved.

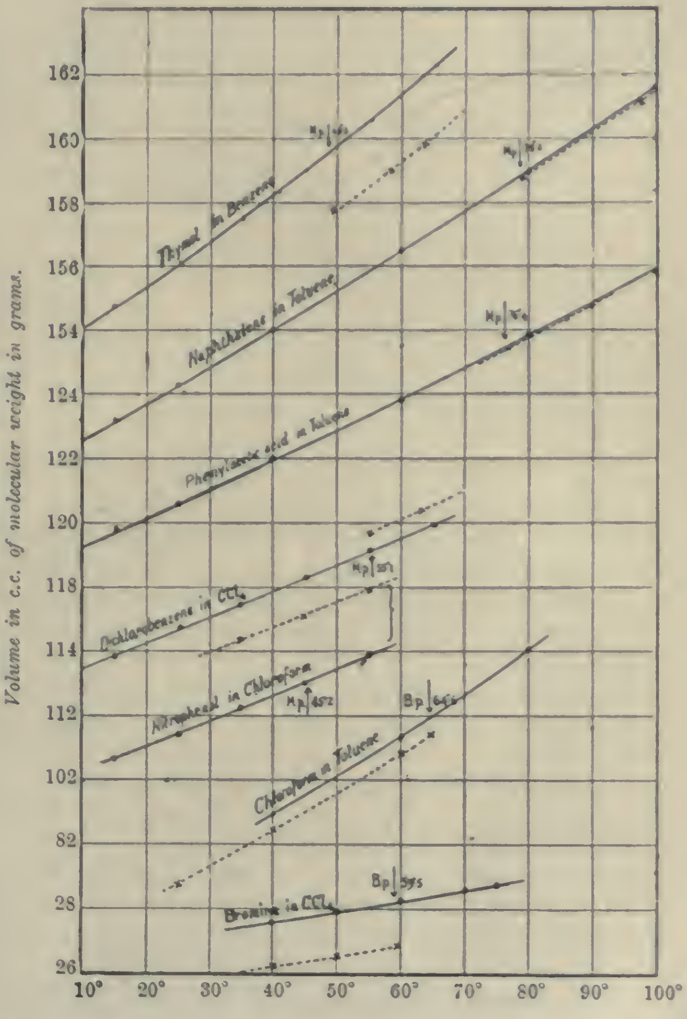
The substances employed in the foregoing experiments had in every case been examined by previous workers and their volumes determined in the liquid state at several temperatures. From these measurements, the molecular volumes were calculated, and the values obtained are given in the last columns of the preceding tables and are indicated on the volume diagram by dotted lines. It is seen that naphthalene and phenylacetic acid dissolved in toluene have volumes in solution almost identical with their volumes as pure liquids; bromine in carbon tetrachloride, thymol in benzene, and chloroform in toluene show greater volumes in solution, whilst nitrophenol in chloroform and dichlorobenzene in carbon tetrachloride have smaller volumes when dissolved.

Two liquids may therefore be mixed without any change of volume taking place, but usually mixing is attended either by a small contraction or a small expansion.

Some very accurate experiments on the mixing of carefully purified

FIG. 1.

Molecular volumes of various substances in solution.

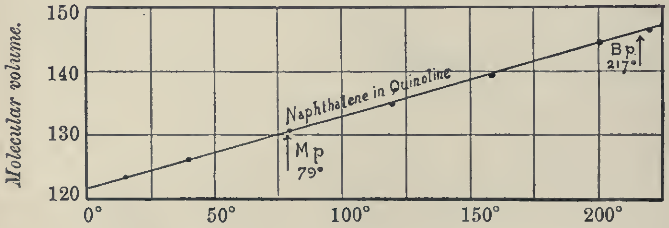


liquids are recorded by Young and Fortey (Trans., 1902, 81, 742 and 772; 1903, 83, 45), and by Thorpe and Rodger (Trans., 1897, 71, 367), and in order to indicate the extent of the change of volume accompanying mixing, I give the measurements made by these investigators:

Mixtures of	Volumes.	Instead of 100 c.c.	Observers.
Toluene and ethylbenzene	Equimolecular	99·966	Y. & F.
Hexane and octane	,,	99·966	,,
Carbon tetrachloride and benzene	,,	99·849	,,
,, ,, ,, methyl alcohol	,,	99·820	,,
Ethyl acetate and ethyl propionate	,,	100·015	,,
Benzene and toluene	,,	100·161	,,
Chlorobenzene and bromobenzene	,,	100·000	,,
Benzene and ethyl alcohol	31 per cent. alcohol	100·000	,,
Ether and chloroform	84 per cent. chloroform	99·185	T. & R.
Carbon disulphide and methyl iodide	78·4 per cent. methyl iodide	100·217	,,

FIG. 2.

Molecular volume of naphthalene in quinoline.



In no case do these measurements by Young and Fortey indicate a change of volume on mixing as great as one-fifth of 1 per cent., and according to Thorpe and Rodger, a mixture of the two dissimilar liquids, ether and chloroform, is accompanied by a change which does not exceed 1 per cent.

Referring again to the volume diagram it will be observed that the curve indicating the volume of the pure liquid at different temperatures runs parallel with the curve showing the volume of the substance in solution. One learns from this that whatever change takes place on mixing two liquids at one temperature, the same amount of change will take place on mixing them at another temperature. It also leads to a second important generalisation: if the volume of a pure substance over the range of temperature when it is liquid can be represented by a curve which coincides with or runs parallel to the volume curve of the substance in solution, then, as the trend of the solution curve is regular, it may safely be concluded that if the pure substance remained liquid, its volume, at any temperature below or above the temperature of the normal liquid state, would be represented by a point on an extension of the liquid volume curve continued parallel to the curve of the volume in solution.

It follows directly from this that, if the two curves coincide, the conditions of the law of liquid volume are fulfilled, and the law may be stated thus: *When a substance in the liquid state dissolves without change of volume, the same substance when in the state of solid or gas will, when dissolved in the same solvent, change to the volume which the same weight of it would have if it were a pure liquid at the temperature of solution.* Should, however, the two curves run parallel, the deviation from the law may be expressed as follows: *When a substance in the liquid state, on being dissolved, changes in volume by a certain amount, the same substance, when in the state of solid or gas, will, when dissolved, assume a volume which differs from the volume which it would have if liquid at the same temperature, by the same amount.*

These two definitions may be combined in a general statement: the volume occupied by a substance in solution is the same as that of the pure substance at the same temperature if it were liquid; or if it is not identical, it deviates by the same amount at all temperatures.

When two pure liquids were mixed it was seen that the change in volume was very small, and the deviation from conformity with the law of liquid volume can in no instance be considerable, yet it seemed of interest to inquire further concerning the cause of the change of volume when two liquids are brought together.

The cause must be looked for in the distribution of the particles of the solute throughout the solvent producing an adjustment of spacing, since it might be expected that molecules differing in size, shape, and weight, when mixed, will arrange themselves so that the new volume is not exactly the sum of the volumes added. The change, moreover, cannot entirely be ascribed to the dissolved substance; the solvent must also be affected, and if that is the case it is evident that the true volume which a substance occupies when in solution cannot be measured, since the amount of change of each constituent is unknown.

From these considerations it was reasonable to predict that alteration of the amount of solvent and the employment of different solvents would give different values for the volume of a dissolved substance, and the following experiments were made to obtain information on these points. Solutions were prepared containing approximately 5, 10, and 20 molecules of naphthalene in 100 molecules of benzene, toluene, xylene, and carbon tetrachloride. Four pyknometers were employed; one to contain the pure solvent, the others the three solutions made with this solvent. The pyknometers were heated in a thermostat to 15°, removed at the same time to ensure that they were all at exactly the same temperature, dried, and weighed:

Solvent.	Mols. naphthalene.	Naphthalene in grams.	Solvent in grams.	Sp. gr. solvent.	Sp. gr. solution.	Vol. of 128 g. naphthalene.
Benzene	5	2·4151	32·0184	0·8848	0·8938	123·90
	10	2·3258	14·9250	,,	0·9025	123·63
	20	2·0620	7·0862	,,	0·9150	123·48
Toluene......	5	2·0382	29·7285	0·8712	0·8802	123·43
	10	2·1583	15·8576	,,	0·8883	123·30
	20	2·2576	7·6144	,,	0·9046	123·17
Xylene	5	1·9115	30·8078	0·8678	0·8761	123·88
	10	2·0811	16·7844	,,	0·8836	123·69
	20	3·8963	17·7555	,,	0·8940	123·55
Carbon tetrachloride	5	2·1084	54·9772	1·6043	1·5741	121·23
	10	2·7271	32·8754	,,	1·5425	121·46
	20	5·4420	36·2363	,,	1·5006	121·98

These molecular volumes of naphthalene, calculated as before on the assumption that each solvent retains the volume it has in the pure state, show that there is in solutions in benzene, toluene, and xylene a distinct diminution in volume with increase of concentration, whilst in carbon tetrachloride the volume becomes greater as the amount of solvent decreases. Several experiments with carbon tetrachloride gave the same result: a diminution in the volume of the dissolved substance on dilution.

The cause of these changes will be discussed later on.

An experiment was then made in order to find the change in volume of the dissolved substance when different solvents were used. Solutions containing approximately 10 molecules of naphthalene to 100 molecules of benzene, toluene, xylene, and carbon tetrachloride were prepared, these were heated at 15°, removed from the bath at the same moment, and weighed:

	Naphthalene. in grams.	Solvent in grams.	Sp. gr. solvent.	Sp. gr. solution.	Vol. of 128 g. naphthalene.
Benzene.....................	2·8556	19·7194	0·8847	0·9014	123·52
Toluene......................	2·6164	25·8188	0·8708	0·8837	123·55
Xylene	2·3361	19·3979	0·8679	0·8832	123·67
Carbon tetrachloride ...	2·2266	27·4185	1·6043	1·5421	122·57

The volume of naphthalene is seen to be nearly the same in benzene, toluene, and xylene, but there is a great diminution when carbon tetrachloride is the solvent. These experiments prove that the volume occupied by a substance in solution at any given temperature alters with the solvent employed and also with the concentration of the solution.

The foregoing results enable one to form a conception of what takes place when two liquids are mixed.

If a pure liquid is a collection of like molecules which are in constant motion jostling each other and changing their direction and motion at every moment, and that to permit of this jostling there are spaces between the molecules, then the question arises: is the interspace per molecule at the same temperature the same for each liquid? Kopp did not recognise the existence of interspaces, and in the atomic volumes deduced by him are included atom and space, and the sum of the atomic values make up the whole volume of the liquid; but according to Horstmann and Traube there must be added to the sum of the values which they assign to the atoms a co-volume of 25·9 c.c. at 15° in order to obtain the molecular volume, and this co-volume has a higher value as the temperature rises.

Now it is very improbable that the molecular interspaces in different liquids should have the same dimensions. The molecules differ in size, shape, and weight, and any value for the co-volume must be an average number from which the real value may in any given case differ considerably. If, however, the co-volume be different in different liquids, then, when two liquids are brought together, an adjustment of the dimensions of the interspaces will sufficiently account for the change in volume.

With regard to this adjustment, little can be inferred from the size and shape of the molecules, but considering only their mass, the direction of the change of volume may in many cases be explained. It was seen that when naphthalene was dissolved in carbon tetrachloride the volume was smaller than when the solvent was benzene, and that, whilst in carbon tetrachloride the volume diminished on dilution, in benzene the volume was greater as the amount of solvent was increased.

When the molecules of naphthalene were introduced amongst the heavier molecules of carbon tetrachloride they would be subjected to greater pressure than if they existed as liquid naphthalene, since the mass attraction between the molecules of carbon tetrachloride is greater than between naphthalene molecules. This cause would lead to a diminution of volume. At the same time the carbon tetrachloride molecules would be separated from each other by the intrusion of the naphthalene molecules; their mutual attraction would be diminished and expansion would result. The latter action must be the smaller since the experiment showed a contraction on mixture.

When more solvent was employed, the separated naphthalene molecules would be subjected to still greater attraction by the heavy carbon tetrachloride molecules and thus produce the diminution which was noticed on dilution.

In the case of naphthalene in benzene, the dissolved molecules are the heavier, they would be under less pressure than if in liquid naphthalene, and this would permit expansion; at the same time the naphthalene molecules would be separated from each other, their mutual attraction would be diminished, and further increase of volume would take place. On adding more solvent the naphthalene molecules would become still more widely separated, their attraction for each other would again be lessened, and the expansion which was noticed on dilution would be brought about.

Observed changes in volume may therefore in many cases be accounted for by the mass attraction between the molecules of solvent and solute, but the shape and size of the molecules which are brought together must also affect the adjustment. Speaking generally, when the molecules of two substances resemble each other in size, shape, and weight, there will be little change on mixing, but when there is marked difference in the structure and weight of the molecules a considerable change may be expected.

The following is an illustration: methyl iodide was dissolved in carbon tetrachloride and in benzene and the molecular volumes determined:

Solvent.	Wt. of methyl iodide.	Wt. of solvent.	Sp. gr. solvent.	Sp. gr. solution.	Vol. of 141·97 g. methyl iodide.
Benzene....................	10·0459	26·5893	0·8847	1·0607	63·37
Carbon tetrachloride ...	6·8050	39·5385	1·6043	1·6778	62·09
Methyl iodide	—	—	2·2924	—	61·93

The volume of the pure methyl iodide is seen to differ very little from its volume in carbon tetrachloride, but the increase in volume is very marked when solution is in the much lighter liquid benzene.

One point in the preceding investigation demands notice: it was assumed as true that the curve of the volume of the substance in solution coincided with or ran strictly parallel to the curve of volume of the pure substance. The experimental results indicate that this is the case, and the examination of some measurements made by Thorpe and Rodger (Trans., 1897, 71, 367) on the densities of mixtures of carbon tetrachloride and benzene and carbon disulphide and methyl iodide leads also to the conclusion that when definite weights of two liquids are mixed the amount of change of volume which occurs at one temperature is the same as the change at another temperature. But it is improbable that any such regularity should hold; for when two liquids have different rates of expansion the amount of change of volume on mixing must vary somewhat with the temperature. As this variation has not been experimentally noticed, one must conclude that it is very small, more especially when the dissolved substance bears no great proportion to the total volume, and it cannot be of sufficient magnitude to invalidate the law of liquid volume which is based on the parallelism of the volume curves.

In the foregoing discussion, proof has been adduced that the true volume of a dissolved substance cannot be known, and that the volume varies with the solvent and with the concentration of the solution; but it has also been shown that the change in volume when two liquids are mixed is very small, and that the volume assumed in solution by a solid, liquid, or gas is never far removed from the volume that the same weight would occupy if liquid at the same temperature. The law of the liquid volume of a dissolved substance is therefore seldom strictly accurate, but it deviates so little from the truth that it deserves a definite position as a guide when dealing with problems relating to solutions in liquids where dissociation cannot take place.

UNIVERSITY COLLEGE,
DUNDEE.

IV.—*The Influence of Light on Diazo-reactions. I.*

By KENNEDY JOSEPH PREVITÉ ORTON, JOSEPH EDWARD COATES (and, in part, FRANCES BURDETT).

THE voluminous literature of the diazo-group does not indicate that the remarkable effect of light on certain reactions of this class of compounds has been closely investigated, notwithstanding the fact that more than one "diazo-type" photographic process has been patented.*

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* Feer (D.R.-P. 53455) patented a process in which a film, coated with a mixture of a diazosulphite and a phenol or an amine, was exposed to light. A decomposition of the former occurred, which was followed by coupling with the phenol or amine, and hence the production of a coloured negative. The unchanged sensitive material was washed away after exposure.

Green, Cross, and Bevan (D.R.-P. 56606; *Ber.*, 1890, **23**, 3131; and *J. Soc. Chem. Ind.*, 1890, **9**, 1001) brought forward a method for the use of the diazo-derivative of primuline for a similar purpose. A "negative" was obtained by exposing films coated with the diazo-compound, the decomposition of which was proportional to the intensity of the light. A "positive" was developed by treatment with an amine or a phenol. In regions of faint illumination, where the diazo-compound had not been decomposed, a colour developed; where the illumination had been intense, all the diazo-compound had been decomposed and the positive was colourless.

They further established that the red end of the spectrum was the more active, and that nitrogen was evolved from the diazo-compound. They, however, express themselves as "undecided whether the product is a phenol, ... or whether the primuline residue enters the molecule of cellulose." They conclude, moreover, "that molecular union with the medium is a necessary condition, ... for the free diazoprimuline, when exposed to light in a thin film is either not decomposed at all, or only after very prolonged exposure."

Ruff and Stein (*Ber.*, 1901, **34**, 1668), using a similar photographic method, have

In the course of an investigation of some reactions of *s*-trisubstituted diazobenzenes, notably *s*-tribromodiazobenzene (Orton, Trans., 1903, **83**, 796; 1905, **87**, 99), it was observed that the diazonium salts, the hydrogen sulphate, and the nitrate, both as solid and in solution, were exceedingly sensitive to light. The instability was the more remarkable, inasmuch as this type of diazonium salt is singularly permanent at the ordinary temperature. The effect of exposure to light could accordingly be most easily demonstrated and studied in the case of such *s*-trisubstituted diazonium salts.

The nature of the decomposition of the diazonium salt depends on the solvent. In water, a phenol is formed; in methyl alcohol, a methyl ether, $\mathrm{Ar{\cdot}O{\cdot}CH_3}$; in ethyl alcohol, an ethyl ether, $\mathrm{Ar{\cdot}O{\cdot}C_2H_5}$, and in acetic acid, the phenyl acetate, $\mathrm{Ar{\cdot}O{\cdot}CO{\cdot}CH_3}$; thus, for example:

$$\mathrm{Ar{\cdot}N(HSO_4){\vdots}N + CH_3{\cdot}CO_2H = Ar{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2SO_4 + N_2}.$$

If the salt is a chloride or a bromide, the diazo-group is also replaced to some extent in aqueous solution by chlorine or bromine.

The influence of light is well illustrated by the behaviour of dilute solutions of 5-bromo-*m*-xylene-, or 6-bromo-ψ-cumene-diazonium hydrogen sulphates. Solutions of these salts can apparently be preserved indefinitely at the ordinary temperature if light is rigidly excluded; thus in ten weeks no measurable volume of nitrogen was evolved from a 1 per cent. solution of either of these salts. If such solutions are boiled, transformation to the corresponding phenols is rapid and quantitative. Exposure to diffused daylight is followed by evolution of nitrogen; in direct sunlight, the speed of the reaction is considerable and the yield of phenol quantitative.

The case of *s*-tribromodiazobenzene is of particular interest, inasmuch as it has been shown, by all who have investigated this substance, to behave abnormally when its solutions in water, in methyl or ethyl alcohol, or in acetic acid are heated. Silberstein (*J. pr. Chem.*, 1883, **27**, 113) could isolate no *s*-tribromophenol in the decomposition of aqueous solution of the diazonium nitrate. Hantzsch (*Ber.*, 1900, **33**, 2517) confirmed this observation, and, in addition, ascertained that no *s*-tribromophenyl methyl- or ethyl-ether was formed on heating the solutions in the corresponding alcohols, *s*-tribromobenzene being the sole product. Similarly, he detected no *s*-tribromophenyl acetate in the reaction with acetic acid, *s*-tribromobenzene again being alone isolated.

The changes which occur when aqueous solutions of these tribromo-

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investigated the effect of the constitution of the diazo-compound on its "sensitiveness." On the basis of some experiments of Andresen (*Photographische Correspondenz*, 1895), they conclude that the diazo-compound undergoes the phenolic decomposition.

benzenediazonium salts * are heated were first described by one of us (Trans., 1903, **83**, 802); it was found that the diazonium salt mainly decomposed into dibromoquinonediazide, bromine appearing in the ionic condition, thus:

$$C_6H_2Br_3\cdot N(HSO_4)\vdots N + H_2O = O_2\colon C_6H_2Br_2\colon N_2 + HBr + H_2SO_4.$$

In the course of this research, this reaction has been again investigated, the diazonium salts being now also heated in solution in 63 per cent. sulphuric acid, a method first employed by Heinichen in the preparation of 2:6-dibromophenol (*Annalen*, 1889, **253**, 281). Although such *s*-trisubstituted benzenediazonium salts, as those obtained from 3:5-dibromo-*o*-toluidine and 3:5-dibromo-*p*-toluidine, which do not undergo the phenolic decomposition when their aqueous solutions are heated, are nearly quantitatively converted into the corresponding cresols, if 63 per cent. sulphuric acid is used as a medium, yet *s*-tribromodiazobenzene is still refractory. The diazonium hydrogen sulphate was rapidly decomposed, but no *s*-tribromophenol was formed. Subsequent to the publication of the preliminary notice (Proc., 1905, **21**, 168), Cain and Norman (Proc., 1905, **21**, 206) showed, however, that some 2 per cent. of *s*-tribromophenol could be obtained if the method described in the German patent (D.R.-P. 95339), namely, heating the diazonium salt with dilute sulphuric acid and sodium sulphate, were used. This result has been confirmed by the authors, who have isolated small quantities of *s*-tribromophenol from among the products of decomposition of *s*-tribromobenzenediazonium hydrogen sulphate, when it is treated according to the directions in the patent. The main product of the reaction is a material resulting from a transformation of the quinonediazide, which is itself not permanent under the conditions. The decomposition, in fact, under these conditions mainly follows the course of that of the aqueous solution.

In the face of such observations it was scarcely to be expected that a means of converting *s*-tribromodiazobenzene quantitatively into *s*-tribromophenol could be found. Nevertheless, such a complete conversion of the diazonium salts in aqueous solution is induced by light. Further, both the *s*-tribromophenyl methyl- and ethyl-ethers and *s*-tribromophenyl acetate are produced if solutions in methyl or ethyl (90 per cent.) alcohols or acetic acid are exposed to light. The yield of the phenyl acetate is quantitative, but under the most favourable conditions some 30 per cent. of *s*-tribromobenzene is formed together with the ethers. Solutions of the diazonium salt in methyl or ethyl alcohol differ in some respects. Whilst the solution in methyl alcohol remains unchanged in the dark, that in ethyl alcohol slowly decomposes, but, in marked contrast to the decomposition induced by light, now only *s*-tribromobenzene is formed.

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* The hydrogen sulphate was mainly used, since there is some difficulty in preserving the nitrate; further, the chloride cannot be easily isolated, an acid chloride being precipitated from the acetic acid solution by ether.

Solutions (or suspensions) in several other media have been examined. When dissolved in 95 per cent. sulphuric acid, the phenolic decomposition takes place slowly, no other substance being produced. Solutions in fuming nitric acid appear to behave similarly, but here a secondary reaction, namely, displacement of the bromine by the nitro-group, complicates the phenomenon.

Formic acid solutions yield only *s*-tribromobenzene, thus:

$$C_6H_2Br_3{\cdot}N(HSO_4){:}N + H{\cdot}CO_2H = C_6H_3Br_3 + H_2SO_4 + N_2 + CO_2.$$

In propionic acid, the diazonium salt is insoluble; nitrogen is evolved from the suspension, but the reaction is exceedingly slow.

The diazonium salts of 2 : 4 : 5 : 6-tetrabromodiazobenzene, 2 : 6-dibromodiazobenzene, 2 : 4 : 6-tribromo-3-nitrodiazobenzene, 3 : 5-dibromo-*p*-diazotoluene, and 3 : 5-dibromo-*o*-diazotoluene, in so far as they have been studied, behave in a completely analogous manner.

Aqueous solutions of benzenediazonium salts rapidly change when exposed to sunlight at 0°; nitrogen is evolved and phenol formed, but the decomposition soon comes to a standstill, owing to a dark turbidity arising from some secondary reaction which prevents access of light. This difficulty is not met with in the case of ψ-cumenediazonium salts, which are, moreover, even less stable in aqueous solutions than benzenediazonium salts at the ordinary temperature. When exposed to light at 0°, nitrogen is rapidly evolved, ψ-cumenol being formed, whilst if shielded from light this decomposition is very slow at that low temperature.

In marked contrast to the sensitiveness of the diazonium salts is the stability of solutions of diazotates. Aqueous solutions of sodium *p*-nitrobenzenediazotate, 3 : 5-dibromo-*p*-toluenediazotate, and benzene-*iso*diazotate are unchanged after two or three days' exposure to light. A solution of potassium *s*-tribromobenzenediazotate in methyl alcohol is equally stable.

Investigation of the effect of variation in the concentration and nature of the acid on the decompositions of diazonium salts, which are accelerated by light, has shown that the former (concentration of the acid) has remarkably little influence on the rate of the transformation. Even up to concentrations of 25 per cent., sulphuric acid does not diminish the speed; at a concentration of 30 per cent., a slight decrease is perceptible, but, as mentioned in the foregoing, even solutions in 95 per cent. sulphuric acid yield phenol on exposure to light. The nature of the acid is only of consequence when the acid radicle can itself replace the diazo-group; in the presence of hydrogen chloride or bromide, light hastens not only the conversion into phenol, but also the replacement of the diazo-group by chlorine or bromine.

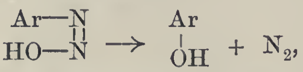
The most marked effect of the presence of acids is seen in the case of those halogendiazobenzenes which tend to undergo another decomposition, namely, the formation of a quinonediazide with the elimination of halogen. This reaction is markedly accelerated by light, and consequently takes place in solutions of diazonium salts exposed to light concurrently with the phenolic decomposition; the latter, however, is always the dominant reaction. Thus it was found that from a 1 per cent. solution of *s*-tribromobenzenediazonium acetate, the amount of bromine eliminated in a given time on exposure to light was three times that set free in a similar solution kept in the dark. No phenol was formed in the latter solution, whereas, in the former, 100 molecules of diazo-compound yielded phenol for every 77 which lost an atom of bromine. This acceleration of the quinonediazide reaction is still perceptible in solutions of the diazonium hydrogen sulphate. In a 1 per cent. solution of the diazonium hydrogen sulphate, the proportion of molecules yielding phenol to those giving quinonediazide is 100 : 25, in a 15 per cent. solution of sulphuric acid it has fallen to 100 : 12, whilst in a 30 per cent. solution the elimination of bromine is no longer perceptible.

The rate at which the decomposition proceeds on exposure to light is greatly influenced by the extent to which the quinonediazide reaction is occurring, for the reason that, when exposed to light, all quinonediazides rapidly change into deeply-coloured, amorphous solids, which, remaining suspended in the solution, effectually prevent the access of light.

According to the view previously explained (Orton, Trans., 1903, 83, 796), the quinonediazide is the result of an interaction of diazonium $\{\mathrm{Ar{\cdot}N{\vdots}N}\}''$ and hydroxyl $(\mathrm{OH})'$ ions. As the concentration of acid increases, the concentration of the hydroxyl ions becomes vanishingly small, and the formation of quinonediazide ceases.

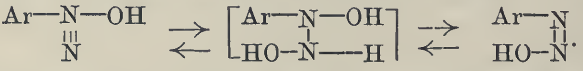
This change accompanying the replacement of the diazo-group by hydroxyl was observed to a greater or less degree in the case of all the halogendiazobenzenes. It is scarcely detectable, if not entirely absent, in the decomposition of 5-bromodiazo-*m*-xylene and 6-bromodiazo-ψ-cumene, is noticeable in that of the two 3 : 5-dibromodiazotoluenes, and assumes still larger proportions as the number of negative bromo- and nitro-groups in the benzene nucleus is increased, until in the case of an aqueous solution of 2 : 4 : 6-tribromo-3-nitrobenzenediazonium hydrogen sulphate 46—47 per cent. of one atomic proportion of bromine is eliminated.

A suggestion as to the mechanism of the transformation of diazonium salts into phenols, which has attained considerable acceptance, was first given by Hantzsch (compare "Diazo-Verbindungen," Ahrens' Sammlung), who represents the phenols as being primarily formed from the *syn*-diazohydroxides, thus:



$$\begin{matrix}Ar-N\\ \|\\ HO-N\end{matrix} \longrightarrow \begin{matrix}Ar\\ |\\ OH\end{matrix} + N_2,$$

by an "intramolecular decomposition" which is comparable to the decomposition of the *syn*-aldoximes into water and nitriles. Since solutions of the diazonium salts are particularly liable to this reaction, he accounts for the *syn*-diazohydroxide, which must on this view be present in such solutions, by the existence of a certain amount of hydrolysis of the diazonium salt. The free diazonium hydroxide formed in this manner has been shown (Hantzsch and Davidson, *Ber.*, 1898, **31**, 1612) to change partially into the isomeric *syn*-diazohydroxide, so that an equilibrium exists which can be represented thus:



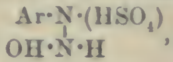
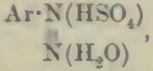
$$\begin{matrix}Ar-N-OH\\ \equiv\\ N\end{matrix} \;\rightleftarrows\; \left[\begin{matrix}Ar-N-OH\\ |\\ HO-N-H\end{matrix}\right] \;\rightleftarrows\; \begin{matrix}Ar-N\\ \|\\ HO-N\end{matrix}.$$

The hydrated compound is suggested as an intermediate step.

It should follow, therefore, that all conditions which favour hydrolysis, for example, diazonium salts of weak acids or the salts of a weak diazonium base, should increase the speed of the phenolic decomposition; further, the presence of an excess of a strong acid should prevent or at least decrease the rate of this transformation.

It was shown, however, by Euler (*Annalen*, 1902, **325**, 292) that the rate of the conversion of diazonium salts into phenols was independent of the presence of excess of acid, at least in dilute aqueous solution. Euler maintains, therefore, that the conversion into phenol can be a purely diazonium reaction, and is not confined to *syn*-diazohydroxides. Recently (*Ber.*, 1904, **37**, 1087), Hantzsch has accepted this correction, and states that he is now of Euler's opinion.

The experiments described in this paper afford independent evidence for the view that diazonium salts in aqueous solution are directly transformed into phenols. As has been shown, the presence of a considerable excess of acid is no hindrance to the change; under the influence of light the reaction takes place at the ordinary temperature in 30 per cent. sulphuric acid, with no decrease of speed. Moreover, it will even proceed, though but slowly, in a 95 per cent. solution of sulphuric acid; in such a medium, it is difficult to imagine even a vanishing trace of hydrolysis. Further, in the light of the experiments here recorded, there would appear to be little reason to think that the other decompositions, namely, the reaction with methyl or ethyl alcohols or with acetic acid, which lead respectively to ethers and acetic esters, are reactions of *syn*-diazo-compounds and not of diazonium compounds. These transformations appear to be regarded by Hantzsch (*loc. cit.*, p. 68 *et seq.*) as decompositions of a *syn*-diazo-compound. The presence of excess of acid is, in these reactions, however, not without effect, in that the product of the reaction induced by light is modified; whereas, under all conditions yet investigated, *s*-tribromobenzene always accompanies the *s*-tribromophenyl methyl- and ethyl-ethers, the proportion of the former is increased in strongly acid solution. In any case, the fact that excess of acid favours the replacement of the diazo-group by hydrogen affords strong evidence that this transformation, at least, is a reaction of the diazonium compound. Possibly the experiments which are now in progress on the accelerating influence of light on the replacement of the diazo-group by chlorine or bromine may illuminate further the mechanism of these diazo-reactions.

With regard to the mechanism of the action of light, it may be suggested that the solvent becomes associated with the diazonium salt (or in dilute solutions, with the diazonium ion). Considering how freely formulæ for hypothetical intermediate products in diazo-reactions have been brought forward in recent years, it is, perhaps, hazardous to attempt to represent graphically this additive product. But in any case it would seem that the quinquevalent "basic" nitrogen atom, which is linked to the acid radicle, cannot be directly involved, or undergo a change of valency, if the reactive compound is a diazonium derivative. From this point of view the expression,  $\begin{array}{l}Ar{\cdot}N{\cdot}(HSO_4)\\ \quad | \\ OH{\cdot}N{\cdot}H\end{array}$, is not admissible, whereas the formula,  $\begin{array}{l}Ar{\cdot}N(HSO_4)\\ \| \\ N(H_2O)\end{array}$, in which the residual valency of the tervalent nitrogen is brought into play, is open to less objection. Such a complex may be supposed to be unstable, breaking up either under the influence of light or heat, yielding a phenol and nitrogen.* Further, it may be supposed that in the case of certain diazonium salts, such as those with several negative substituents, *s*-tribromodiazobenzene and the like, this unstable complex may be resolved on mere heating into its constituents, water and diazonium salt, a fact which would account for the difficulty of converting the diazo-compound, just named, into the corresponding phenol. From the foregoing it is obvious that if such a complex exists, its formation is not materially affected by the presence of acid.

The reactions of *s*-tribromobenzenediazonium hydrogen sulphate

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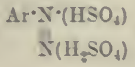
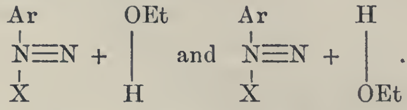
* Perhaps in solution in sulphuric acid, a complex  $\begin{array}{l}Ar{\cdot}N{\cdot}(HSO_4)\\ \| \\ N(H_2SO_4)\end{array}$ is the sensitive material.

with ethyl alcohol (or methyl alcohol or acetic acid) are of particular interest in this connexion. Hantzsch (*loc. cit.*, p. 73) has suggested that the two different reactions of diazonium compounds with ethyl alcohol, the formation of an ethyl ether, or the replacement of the diazo-group by hydrogen, are due to two different additive compounds, which are stereoisomeric, thus:—



$$\begin{array}{c}\text{Ar}\\|\\\text{N}\\|\\\text{X}\end{array}\!\!\equiv\text{N} + \begin{array}{c}\text{OEt}\\|\\\text{H}\end{array} \quad\text{and}\quad \begin{array}{c}\text{Ar}\\|\\\text{N}\\|\\\text{X}\end{array}\!\!\equiv\text{N} + \begin{array}{c}\text{H}\\|\\\text{OEt}\end{array}.$$

The formation of *s*-tribromobenzene alone from the corresponding diazonium salts is ascribed to the fact that the presence of the three negative bromine atoms in the benzene nucleus allows only of the formation of one type of addition, namely, the latter, in the decomposition of which the hydrogen remains combined with the phenyl nucleus. Accepting the view that the existence of two different additive products underlies the two different reactions, the decomposition in light shows that, contrary to Hantzsch's opinion, both are produced from *s*-tribromobenzenediazonium salts and ethyl alcohol. It is possible that one only persists at higher temperatures; or, since at the ordinary temperature *s*-tribromobenzene is alone produced in the dark, the two additive compounds are formed in very different proportions, that which yields the ether being possibly the more sensitive to light. The effect of excess (or high concentration) of acid, which is to reduce the proportion of ether, could then also be interpreted as due to a prevention of the formation of the corresponding additive compound.

The acceleration of the replacement of bromine by hydroxyl (quinonediazide reaction) cannot be considered as analogous to the reactions described above, since this change involves changes in the benzene nucleus. It is more probably related to the conversion of azoxybenzene into hydroxyazobenzene, which Lobry de Bruyn noticed was induced by light.

EXPERIMENTAL.

s-*Tribromodiazobenzene.*

Aqueous solutions of the pure salts of *s*-tribromodiazobenzene are quite colourless, but are extremely sensitive to light; even on momentary exposure to direct sunlight a 1 per cent. solution assumes a yellow tint and becomes faintly turbid. Diffused daylight and even gaslight have the same effect, but in a less degree. On the other hand, such solutions can be kept in the dark room for days without appreciable change, although in time (after several days) bromine ions can be detected in the solution (compare *Proc. Roy. Soc.*, 1902, 71, 157).

Solutions in methyl or ethyl (90 per cent.) alcohols or in acetic acid are equally sensitive, although, owing to the solubility of the products of decomposition, the rapid change is only made obvious by the evolution of nitrogen when the flask containing the solution is connected with a nitrometer.

In the case of this and similarly constituted diazonium salts, the decomposition of the aqueous solution pursues two courses, the main reaction results in the formation of *s*-tribromophenol, nitrogen being evolved; at the same time, however, bromine is eliminated in the ionic condition, and a quinonediazide produced. The last-mentioned compound is itself changed by light, being transformed into a dark brown, amorphous powder. For the reasons given in the introduction, the presence of excess of acid should reduce the proportion of the subsidiary reaction whatever effect such an increase in acidity had upon the phenolic decomposition. The latter change can therefore be best followed in acid solution.

On exposing a 1 per cent. solution of *s*-tribromobenzenediazonium hydrogen sulphate in 15 per cent. sulphuric acid to direct sunlight, a white solid which consisted of minute crystals was deposited, whereas in the absence of the acid a dark brown material separated. The solid was collected, washed, and extracted with sodium carbonate, which left, in the case of the aqueous solution, a considerable quantity of brown solid undissolved. The phenol was precipitated from its solution in alkali and dissolved in dilute alcohol, from which it crystallised in long, slender needles melting at 92°; its melting point was unchanged by admixture with a specimen of *s*-tribromophenol:

0·1925 gave 0·3262 AgBr. Br = 72·12.

$C_6H_3OBr_3$ requires Br = 72·50 per cent.

Effect of the Concentration of the Sulphuric Acid on the Decomposition of the Diazonium Salt under the Influence of Light.—The salt appears to decompose most rapidly, as estimated by the evolution of nitrogen, in the presence of a 15—30 per cent. sulphuric acid. At lower concentrations, the evolution of nitrogen is slower, but the retarding influence may be due to the dark precipitate, which acts simply by preventing the light from gaining access to the liquid. At higher concentrations, the decomposition is again retarded, but the phenol is formed even in solutions in concentrated (95 per cent.) sulphuric acid.

The following results will show the quantitative relation existing between the two reactions, the elimination of bromine and the phenolic decomposition, in different concentrations of sulphuric acid.

(i) On exposing 50 c.c. of a 1 per cent. solution of the diazonium hydrogen sulphate for forty-eight hours (in October), 55 per cent. of the salt was decomposed, 11·8 c.c. of nitrogen were evolved, and the liquid yielded 0·0249 gram of silver bromide. Ratio of the number of molecules yielding phenol and nitrogen to the number giving quinonediazide and bromine = 100 : 25.

(ii) Two exactly similar experiments were made, using a 15 per cent. solution of sulphuric acid instead of water as solvent. (*a*) Eighty-six per cent. of the salt was decomposed, 21 c.c. of nitrogen were evolved, and the liquid yielded 0·0212 gram of silver bromide. (*b*) Sixty-six per cent. of the salt was decomposed, 16·5 c.c. of nitrogen were evolved, and the liquid yielded 0·0176 gram of silver bromide. The ratio of the two decompositions was in each case 100 : 12.

In these experiments, the volume of the gas could only be approximately measured, and, further, it is assumed that nitrogen is formed only from the phenolic decomposition, an assumption which was shown to be justified by direct estimation (weighing) of the phenol. The unchanged diazo-compound was weighed as β-naphthol derivative, and hence the percentage of decomposed salt was obtained.

Effect of Temperature on the Velocity of Decomposition.—There are great difficulties in the way of determining the velocity of a reaction which depends on the varying illumination of the sun. The difficulties are increased in the case of the phenolic decomposition of the diazonium salts by the precipitation of tribromophenol, which acts as a screen to the solute yet undecomposed.

Attempts were made to ascertain the effect of temperature. Equal amounts of two 1 per cent. solutions of the diazonium salt in 15 per cent. sulphuric acid were exposed in similar flasks attached to nitrometers. One flask was immersed in ice and water, and the other in water at a given temperature, great care being taken that each flask was equally exposed to light. In these circumstances all irregularities in the illumination affected each solution equally. The progress of the decomposition was estimated by measuring the nitrogen evolved. Several experiments were made; the following will illustrate the difference of temperature.

Experiment I.—Flask *A*, temperature 17°, 50 per cent. of the diazonium salt was decomposed in two hours fifty minutes; flask *B*, temperature 2°, 50 per cent. decomposed in four hours.

Experiment II.—Flask *A*, temperature 20°, 50 per cent. of the diazonium salt was decomposed in one hour forty-two minutes; flask *B*, temperature 2°, 50 per cent. of the diazonium salt was decomposed in two hours twenty minutes. In this experiment the illumination was more intense than in Experiment I.

Action of Light on s-Tribromobenzenediazotate.—A solution of the diazotate was prepared by adding 0·25 gram of diazonium salt dissolved in 25 c.c. of water to 13 c.c. of a 10 per cent. solution of sodium hydroxide. The solution was exposed to sunlight on two successive days. Nitrogen was not evolved nor was bromine eliminated; the solution, moreover, remained colourless.

Attempts to obtain s-*Tribromophenol by Boiling Aqueous Solutions of the Diazonium Salts.*

It has frequently been observed that substituted benzenediazonium salts do not yield phenols, or at least only in small quantities, when the aqueous solutions of their salts are boiled. In the case of *s*-tribromobenzenediazonium hydrogen sulphate it has previously been shown that bromine is eliminated, and a dibromoquinonediazide formed, at least in the first instance (Orton, Trans., 1903, **83**, 802); no *s*-tribromophenol was discovered. The decomposition of aqueous solutions of this salt has now been more exactly followed. Solutions varying in concentration from 1 to 10 per cent. were heated at 100° in an apparatus from which the air had been expelled by carbon dioxide, so that the nitrogen evolved could be measured. Decomposition was complete in two hours; from 75 to 80 per cent. of the total nitrogen was evolved, the lower number being obtained from the more concentrated solutions. No diazonium salt remained undecomposed, but the yellow liquid contained quinonediazide, which could be extracted with chloroform and coupled in the usual way with β-naphthol (compare Orton, Trans., 1905, **87**, 104). From 58—60 per cent. of one atomic proportion of bromine was found in the solution. The solid product of the reaction was a brown, amorphous powder, which contained small amounts of dibromoquinonediazide, and *s*-tribromobenzene. Both these could be extracted with alcohol, but the main part of the solid was insoluble in that solvent.

The addition of reduced copper accelerated the evolution of nitrogen, but did not otherwise appear to affect the course of the decomposition.

Since it has been noted by Heinichen (*Annalen*, 1889, **253**, 281) and others that the phenolic decomposition takes place more readily in fairly concentrated solutions of sulphuric acid, for example, in a solution of sulphuric acid boiling at 150°, attempts were made to obtain *s*-tribromophenol by using 50—63 per cent. sulphuric acid as solvent. No *s*-tribromophenol could be obtained from the product of decomposition; but a very little *s*-tribromobenzene was isolated. In the case of the 50 per cent. acid, only about 3 per cent. of one atomic proportion of bromine was eliminated, but from the 63 per cent. acid, which boils at 150°, as much as 35 per cent. was found, a difference which was probably to be attributed to the higher temperature. In all cases, the acid mother liquor was bright yellow, and contained quinonediazide.*

Decomposition of the Dry Diazonium Salt.—The diazonium hydrogen sulphate (1 gram) was placed in a desiccator containing phosphorus pentoxide, and kept evacuated in the dark for twelve hours. On exposure to sunlight, the salt became discoloured, and, after a few hours, of a chocolate-coloured hue. On examination, it was found that the surface only had been affected, the dark solid was insoluble in water, and thus could be freed from the unchanged diazonium salt. It was found to contain halogen but no nitrogen; it was insoluble in alkali hydroxide, and in the usual organic solvents with the exception of glacial acetic acid, in which it could, at least partly, be dissolved. The quantity was too small to admit of further investigation.

Acceleration of the Elimination of Bromine by Light.—The experiments were made with *s*-tribromobenzenediazonium acetate, which undergoes the quinonediazide decomposition at a convenient rate (Orton, *loc. cit.*).

A 1 per cent. solution of the diazonium hydrogen sulphate (0·25 gram) containing three equivalents of sodium acetate was exposed for five hours to the light in a flask attached to a nitrometer. A bulky, brown solid separated, and a small amount (4·6 c.c.) of nitrogen was evolved. 27·6 per cent. of one atomic proportion of bromine (AgBr = 0·0296 gram) was eliminated. The ratio of the number of molecules undergoing the phenolic decomposition to those undergoing the quinonediazide decomposition is therefore 100 : 77. An exactly similar solution kept in the dark for the same period evolved no nitrogen; the solution became yellow in colour, and a slight yellow precipitate formed. Ten per cent. of one atomic proportion of bromine (AgBr = 0·0108 gram) was eliminated. Repetitions of the experiment gave a similar result. As was to be expected, variations in the intensity of light affected the phenolic decomposition to a greater extent than the quinonediazide decomposition.

Decomposition of s-*Tribromobenzenediazonium Hydrogen Sulphate in Methyl Alcoholic Solution.*—The diazonium salt is readily soluble in methyl alcohol, and the solution when kept in the dark is stable;

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* Dr. J. C. Cain drew the author's attention to the fact that the method of inducing the phenolic decomposition by heating the diazonium salt in a saturated solution of sodium sulphate was effective in converting a small proportion of *s*-tribromobenzenediazonium hydrogen sulphate into *s*-tribromophenol. An experiment was tried, using 10 grams of the diazonium salt in a solution made up of 14 c.c. of sulphuric acid and 32 c.c. of water, 18 grams of hydrated sodium sulphate being added. The mixture was distilled in a slow current of steam, the flask being heated in an oil-bath. A small quantity of *s*-tribromophenol (m. p. 88°) mixed with another substance melting at 75—76°, which does not dissolve in aqueous sodium carbonate, was obtained.

thus no nitrogen was given off from a 1 per cent. solution which was kept in the dark for twenty-eight hours (temperature 10·5°); but on exposure to sunlight for one hour 72 per cent. of the salt was decomposed. On again placing this solution in the dark, decomposition ceased.

Although solutions in methyl alcohol at the ordinary temperature are stable if screened from light, decomposition rapidly occurs if the solution is boiled, *s*-tribromobenzene being alone produced.

The main decomposition under the influence of light is accompanied by a small amount of a secondary reaction, namely, the elimination of bromine, and the formation of a quinonediazide. The decomposition of the latter in light causes the solution to become deeply coloured. The solid product of the reaction which remains in solution in the methyl alcohol was obtained by evaporating the solvent after decomposition had been completed, sodium carbonate having been added to neutralise the free sulphuric acid. The solid residue, which was highly coloured, was distilled in steam; from the colourless solid distillate a small quantity of *s*-tribromophenol was extracted by sodium hydroxide. It melted at the correct melting point, 95°. The main portion of the solid, which was insoluble in sodium hydroxide, melted at 60—65°. It was thought that this solid was a mixture of *s*-tribromobenzene (m. p. 120°) and *s*-tribromoanisole (m. p. 88°), but crystallisation from alcohol did not change the melting point.* It was therefore treated with hydriodic acid in order to convert the ether into *s*-tribromophenol. From the product both *s*-tribromobenzene and *s*-tribromophenol were easily isolated, no indications of the presence of a third substance being noticed. The relative proportions of these two substances were determined by estimating the methoxy-group and determining the percentage of bromine in the mixture. The two methods agreed closely, within one per cent., the mixture containing 63—64 per cent. of the ether. The methoxy-group was estimated by Zeisel's method, using a mixture of acetic anhydride and hydriodic acid to decompose the ether; two hours' heating at 160° was found necessary for complete decomposition.

Effect of the Presence of Water or Acids.—Addition of acid or dilution of the methyl alcohol with water does not greatly change the rate of the decomposition in sunlight; in both cases there is a slight decrease. In the presence of acid (15 per cent. H_2SO_4), bromine is not eliminated, and in consequence no colour, owing to the decomposition of quinonediazide, developed.

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* The solubilities of *s*-tribromobenzene and *s*-tribromoanisole are very similar in both methyl and ethyl alcohols. Both are moderately soluble in boiling 90 per cent. ethyl alcohol. At 15°, 100 c.c. of this alcohol dissolves 1·03 grams of the tribromoanisole, and 0·4 gram of the tribromobenzene; these are almost the proportions in which these two substances are found in the product of decomposition of the diazonium salt in methyl alcoholic solution.

The proportion of *s*-tribromobenzene and *s*-tribromoanisole is considerably modified in favour of the former, which now forms the main product of the reaction; *s*-tribromobenzene separates in the pure state during the decomposition. Owing to this effect of acid, high concentrations of the diazonium hydrogen sulphate, 4 per cent. and upwards, yield mainly *s*-tribromobenzene on exposure to light. In such a solution, the concentration of the sulphuric acid is initially decinormal, and as the decomposition proceeds becomes fifth-normal.

Behaviour of Alkalidiazotate in Methyl Alcoholic Solution.—The behaviour of methyl alcoholic solutions of sodium or potassium *s*-tribromobenzenediazotates offers a marked contrast to that of the diazonium salts. A 1 per cent. solution of potassium diazotate remained quite colourless and unchanged during four hours' exposure to light.

Decomposition of s-*Tribromobenzenediazonium Hydrogen Sulphate in Ethyl Alcoholic Solution.*—*s*-Tribromobenzenediazonium hydrogen sulphate is very sparingly soluble in ethyl alcohol at the ordinary temperature, 100 c.c. dissolving somewhat less than 0·2 gram. In 90 per cent. alcohol, on the other hand, the salt dissolves freely.

A suspension of the salt in absolute alcohol changes very slowly at the ordinary temperature when protected from the light, the amount of nitrogen evolved in twenty-four hours being only just detectable. On the other hand, the solution of the salt in 90 per cent. alcohol is unstable even in the dark; a 1 per cent. solution continuously evolves nitrogen (temperature, 11—12°), 50 per cent. of the salt being decomposed in twenty-four hours. *s*-Tribromobenzene is the main product of the change, but at the same time bromine is eliminated, representing about 10 per cent. of one atomic proportion.

On exposure to sunlight, both the suspension of the salt in absolute alcohol and the solution (1 per cent.) in 90 per cent. alcohol decompose very rapidly. Whilst the 90 per cent. alcohol becomes very deeply coloured, the absolute alcohol assumes only a pale yellow tint. The solid products in the two cases do not materially differ, and consisted of *s*-tribromophenetole and *s*-tribromobenzene.

Dilution of the alcohol with water retards the decomposition; thus two similar solutions in 50 per cent. and 25 per cent. alcohol had decomposed respectively to the extent of 82 and 62 per cent. after exposure to diffused daylight for five and a half hours. In both cases, *s*-tribromobenzene was the main product, a small amount of bromine being eliminated.

The effect of the presence of excess of acid was tested by exposing a 1 per cent. solution of the diazonium salt in a 15 per cent. solution of sulphuric acid in 90 per cent. alcohol. The decomposition took place rapidly, the solution acquiring only a pale yellow tint. No bromine was eliminated, and therefore no quinonediazide formed, a result in accord with all previous observations as to the effect of acid on the decomposition of this diazonium salt. Co-related with the non-formation of the quinonediazide is the absence of colour. It is noteworthy that in this case also *s* tribromobenzene is the only product of the reaction.

The foregoing observations indicate that the most favourable conditions for the formation of the phenetole are to be found in the use of pure alcohol and the absence of acid. The preparation in quantity was accordingly carried out by exposing a suspension of the diazonium salt (4 grams) in 100 c.c. of alcohol. When all the solid had dissolved and the evolution of nitrogen had ceased, the solution was evaporated to half its volume, whereupon pure *s*-tribromobenzene (m. p. 119—120°, 1·2 grams) separated. Since *s*-tribromobenzene is but slightly soluble in cold alcohol, almost the whole of this substance is thus found. The mother liquor was then evaporated to dryness and the product recrystallised from alcohol, but such treatment failed to raise the melting point above 60—65°, whereas *s*-tribromophenetole melts at 74°. Control experiments, moreover, showed that it was difficult to isolate from mixtures of *s*-tribromobenzene and the phenetole, and then only with great loss, any pure phenetole. The composition of the mixture was accordingly ascertained from estimations of bromine and the ethoxy group;* both analyses agreed in showing that the mixture contained 70—72 per cent. of the ether. After treating the mixture with hydriodic acid, the resulting *s*-tribromophenol and *s*-tribromobenzene could easily be separated by alkali. From these results it follows that the original mixture of *s*-tribromobenzene and *s*-tribromophenetole contained about 5·7 per cent. of the former.

Decomposition of s-*Tribromobenzenediazonium Hydrogen Sulphate in Acetic Acid Solution.*—*s*-Tribromobenzenediazonium hydrogen sulphate dissolves freely in glacial acetic acid (99 per cent.); the solution is quite stable in the dark at the ordinary temperature, but becomes coloured on boiling, *s*-tribromobenzene being formed. On exposing a solution (1 per cent.) to sunlight, decomposition is rapid and complete; the addition of an equal volume of water causes the separation of colourless needles which melt at 82°, the melting point of *s*-tribromophenyl acetate, $C_6H_2Br_3{\cdot}OAc$. An analysis showed that this substance was quite pure:

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* In order to obtain an accurate estimation of the ethoxy-group in *s*-tribromophenetole by Zeisel's method, very prolonged heating of the substance with hydriodic acid (1 vol.) and acetic anhydride (0·5 vol.) is necessary. Thus, in one determination (*s*-tribromophenetole = 0·3426 gram), ethyl iodide only ceased to be given off after six hours' heating, the percentage of ethoxy-group being found = 11·54, whilst $C_6H_2Br_3 \cdot OEt$ requires 12·19 per cent.

0·2103 gave 0·3186 AgBr. Br = 64·46.

$C_8H_5O_2Br_3$ requires Br = 64·33 per cent.

The effect of diluting the acetic acid or of adding sulphuric acid is to decrease the rapidity of the decomposition, water having the greater influence. The solid product obtained from the dilute acetic acid consisted of a mixture of *s*-tribromophenol and its acetyl derivative in about equal proportions. A small amount of phenol was also present in the product obtained from the mixture of acetic and sulphuric acids.

Decomposition of s-*Tribromobenzenediazonium Hydrogen Sulphate in Various Media.*

Formic Acid.—The diazonium salt is readily soluble in formic acid (90 per cent.); in the dark, the solution was stable, no gas being evolved. On exposure to sunlight, a very rapid decomposition set in; the solid product consisted mainly of *s*-tribromobenzene mixed with a small amount of *s*-tribromophenol; no phenyl formate was discovered. Since the formic acid had acted as a reducing agent, carbon dioxide should be present in the evolved gas. Examination of the gas showed this supposition to be correct.

Propionic Acid.—The diazonium hydrogen sulphate does not perceptibly dissolve in propionic acid. When the suspension is exposed to sunlight nitrogen is slowly evolved, and the solution becomes coloured a deep yellow. Neither *s*-tribromobenzene nor *s*-tribromophenol are formed, but owing to the slowness of the decomposition sufficient material could not be accumulated to determine its identity with tribromophenyl propionate.

Sulphuric Acid.—The diazonium salt is readily soluble in concentrated sulphuric acid (95 per cent.). The colourless solution slowly evolves nitrogen in sunlight. On cautiously diluting the solution, pure *s*-tribromophenol crystallises out free from any trace of by-product.

Nitric Acid.—Fuming nitric acid (sp. gr. 1·5) dissolves the diazonium salt freely. The decomposition in sunlight is complicated by the concomitant decomposition of the nitric acid, and by the interaction of the acid with the primary product, which is probably *s*-tribromophenol. Bromine is partly displaced by the nitro-group, and can be estimated in the solution. It was not possible to isolate a single substance from the mixture of nitrobromophenols, but picric acid appeared not to be present.

Organic Liquids.—The diazonium salt does not dissolve to any extent in glycerol, lactic acid, butyric acid, or ethyl acetoacetate. The suspension in the two solvents first named decomposes fairly rapidly, *s*-tribromobenzene being formed in each case. In the other two media, the decomposition is very slow.

Decomposition of Other Substituted Diazobenzenes.

2 : 6-*Dibromodiazobenzene.*—The behaviour of this diazonium hydrogen sulphate towards light is similar to that of the *s*-tribromo-derivative, and affords an extremely easy method of preparing 2 : 6-dibromophenol. In aqueous solution the decomposition is very rapid, a very small quantity of bromine (2·54 per cent. of one atomic proportion) being eliminated. The phenol was freed from a small quantity of brown solid, the decomposition product of the bromoquinonediazide, by dissolving in sodium hydroxide. The phenol melted at 56° and gave the following numbers on analysis:

0·147 gave 0·2186 AgBr. Br = 63·3.

$C_6H_4OBr_2$ requires Br = 63·5 per cent.

This phenol can also be prepared easily from the diazonium salt by Heinichen's method (*loc. cit.*), using a 63 per cent. solution of sulphuric acid. Decomposition is complete in three-quarters of an hour; the yield is good and no appreciable amount of quinonediazide or other substance seems to be formed.

2 : 3 : 4 : 6-*Tetrabromodiazobenzene.*—In the decomposition of aqueous solutions of this diazonium hydrogen sulphate by sunlight, the quinonediazide decomposition takes a more prominent place, some 15 per cent. of one atomic proportion of bromine being eliminated. The tetrabromophenol which is mainly formed can be obtained in a purer state when the decomposition is effected in 15 per cent. sulphuric acid, the quinonediazide decomposition being then inconsiderable. The phenol melted at 115°:

0·1448 gave 0·2645 AgBr. Br = 77·7.

$C_6H_2OBr_4$ requires Br = 78·01 per cent.

When this salt was heated in 63 per cent. sulphuric acid solution, a rapid and complex decomposition took place. As much as 53·6 per cent. of one atomic proportion of bromine appears in the solution. Very small amounts of two crystalline products were noticed, but no tetrabromophenol was isolated.

2 : 4 : 6-*Tribromo-3-nitrodiazobenzene.*—The decomposition of this diazonium salt, which is very rapid when a $\frac{1}{4}$ per cent. solution is exposed to sunlight, appears to be very complex; 46—47 per cent. of one atomic proportion of bromine is eliminated, and the solid product

is a mixture of the decomposition product of the quinonediazide and the phenol arising directly from the diazonium salt. The addition of sulphuric acid reduced the proportion of the quinonediazide decomposition; nevertheless some 17·8 per cent. of bromine was eliminated.

p-*Nitrodiazobenzene.*—The existence of the remarkably stable *p*-nitrobenzenediazotates and the corresponding nitrosoamine has rendered possible the testing of the action of light on these classes of substances. A dilute aqueous solution of the pure sodium *p*-nitrobenzenediazotate was exposed to light for several days. The liquid darkened slightly, and about 2 c.c. of gas were evolved. Examination of the solution after exposure showed that the diazotate was mainly unchanged.

p-*Nitrophenylnitrosoamine* (*p*-nitrobenzenediazohydroxide), which was prepared by Schraube and Schmidt's method from sodium *p*-nitrobenzenediazotate, is insoluble in cold water and slowly decomposes at the ordinary temperature. In the dark at 0° it is, however, quite stable. A suspension in water was exposed to sunlight in a flask which was immersed in ice and water, the light having access to one side of the flask. The substance rapidly darkened and nitrogen was slowly evolved, 4 c.c. being collected during two hours' exposure.

Decomposition of Diazobenzene in Light.

Inasmuch as acid solutions of diazobenzene readily undergo the phenolic decomposition at the ordinary temperature, testing of the accelerating effect of sunlight on this change was somewhat difficult. Moreover, sunlight produces other changes in solutions of this diazonium salt, which result in causing the liquid to become dark and turbid, effects which prevent light from gaining access to the liquid and thus stop the reaction.

Two exactly similar solutions of the diazonium hydrogen sulphate were made up in 20 per cent. sulphuric acid, and placed in flasks connected with nitrometers. One was exposed to sunlight and the other placed in a dark room, each being immersed in mixtures of ice and water. The solution, which was exposed to sunlight, became dark and turbid, and nitrogen was slowly evolved. The solution in the dark did not change in appearance, but a small volume of nitrogen was evolved, at about a quarter of the rate of the solution exposed to light. The solutions, still thoroughly cold, were extracted with chloroform in order to isolate any phenol. The residues left after evaporating the chloroform were distilled in steam, and the aqueous solutions treated with bromine water. The distillate from the solution which was exposed to light gave a precipitate of *s*-tribromophenol (m. p. 95°), whilst that from the screened solution gave only a slight turbidity.

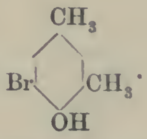
Similar experiments were made with a "normal" diazo-solution, which was made up by adding 25 c.c. of a solution of benzenediazonium chloride (from 1 gram of aniline) to 30 c.c. of a 10 per cent. solution of sodium hydroxide. This solution decomposes when kept in the dark at the ordinary temperature, 25 c.c. of nitrogen being evolved in twenty-four hours. A similar solution, in which, however, 30 c.c. of a 30 per cent. solution of sodium hydroxide were used, instead of the 10 per cent. solution, was more stable, and decomposed very slowly in the dark; light did not appear appreciably to hasten the rate of decomposition.

Decomposition of Methyldiazobenzenes.

5-*Bromo*-4-*diazo*-m-*xylene.*—Unlike other *s*-trisubstituted anilines in which negative groups such as the nitro-group or bromine are present, 5-bromo-*m*-xylidine can be diazotised in dilute acid solution. The solid diazonium salts can be prepared very readily in the usual way.

Aqueous solutions of the diazonium salts are quite stable at the ordinary temperature, provided that they are screened from light. Thus a 1 per cent. solution of the diazonium hydrogen sulphate in 15 per cent. sulphuric acid was kept in a flask connected with a nitrometer for seventy-three days, the temperature ranging from 10—15° during that period. No gas was evolved, but when this solution was exposed to sunlight, a rapid decomposition set in, gas being given off, and an oil separating. No bromine is eliminated and the diazonium salt can be converted quantitatively into the xylenol. This change can be brought about with equal readiness by boiling the aqueous solutions of the diazonium salts. Very different is the behaviour of solutions of the diazotates. In the dark they are quite stable, and when exposed to sunlight only show signs of decomposition if the excess of alkali is slight and consequently the hydrolysis considerable.

5-*Bromo*-m-4-*xylenol*,



This xylenol appears to have been prepared by Noelting, Braun, and Thesmar (*Ber.*, 1901, **34**, 2242) from the corresponding xylidine. These authors state that the xylenol is a solid melting at 72°. We have, however, found that the xylenol obtained from 5-bromo-*m*-4-xylidine by diazotising and then decomposing the diazonium salt either by boiling or by exposing its aqueous solution to light, is an oil at the ordinary temperature. Moreover, bromination of *m*-4-xylenol also yields a monobromo-derivative which is identical with the substance obtained from the bromoxylidine.

Bromination of m-4-*Xylenol.*—A solution of bromine (6·55 grams) in acetic acid was added to a solution of *m*-4-xylenol (5 grams) in the same solvent in which fused sodium acetate (3·6 grams) was suspended. Bromination was instantaneous, heat being developed. The xylenol was separated by addition of water, and distilled in steam, and after separation from the aqueous distillate by chloroform and drying in the latter solvent, the oil was fractionated under reduced pressure. It was colourless, boiled at 110·5° under 18 mm. pressure, and had a sp. gr. 1·4569 at 11°/4°:

0·1235 gave 0·1141 AgBr. Br = 39·89.

C_8H_9OBr requires Br = 39·80 per cent.

The bromoxylenol prepared from the bromoxylidine by way of the diazo-compound, boiled at 112° under 20 mm. pressure, and had a sp. gr. 1·4607 at 11°/4°.

An analysis of a specimen obtained by boiling a solution of the diazonium salt gave the following numbers:

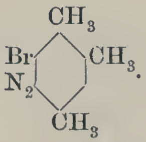
0·1215 gave 0·1145 AgBr. Br = 40·10 per cent.

A specimen obtained by exposing a solution of the diazonium salt to light gave the numbers:

0·1098 gave 0·1018 AgBr. Br = 39·45.

C_8H_9OBr requires Br = 39·80 per cent.

6-*Bromo*-5-*diazo*-ψ-*cumene*,



6-*Bromo*-ψ-*cumidine* (6-*Bromo*-5-*amino*-1 : 2 : 4-*trimethylbenzene*).—This base has apparently hitherto not been described. It is readily prepared by brominating ψ-cumidine in acetic acid solution in the presence of sodium acetate, care being taken to add the solution of the base to the solution of the bromine. The bromo-ψ-cumidine is precipitated by addition of water and purified by distilling in steam. It crystallises from dilute alcohol in long, colourless needles melting at 68—69°:

0·1906 gave 0·1675 AgBr. Br = 37·4.

$C_9H_{12}NBr$ requires Br = 37·4 per cent.

The salts of this base are not markedly hydrolysed by water, thus resembling those of bromoxylidine. It is very readily acetylated by heating for a short time with acetic anhydride at 100°; the *acetyl* derivative crystallises in clusters of four-sided prisms melting at 206°.

It can easily be diazotised in dilute acid solution, and the solid diazonium hydrogen sulphate can be prepared in the usual way.

Acid solutions of bromo-ψ-diazocumene behave in exactly the same way as do those of bromodiazoxylene. Kept in the dark at the ordinary temperature they are quite stable, but on exposure to light, gas is immediately evolved, and a turbidity soon appears in the solution. Pure 6-bromocumenol (m. p. 32—33°) slowly separates in needles. Boiling of the aqueous solutions of the salts brings about a rapid and quantitative conversion into the bromocumenol.

5-*Diazo-ψ-cumene.*—An attempt was made to contrast the decomposition of an acid solution of diazo-ψ-cumene exposed to light with one kept in the dark. At the ordinary temperature, this diazo-compound decomposes fairly quickly, whether screened from light or not. At 0—2°, a marked difference is observed; whilst the solution which is kept in the dark very slowly evolves nitrogen, the other decomposes rapidly. ψ-Cumenol crystallised out as the decomposition proceeded, and melted at 71°.

3 : 5-*Dibromo-*o-*diazotoluene,* and 3 : 5-*Dibromo-*p-*diazotoluene.*—The dibromodiazotoluenes resemble very closely *s*-tribromodiazobenzene. Solutions of the hydrogen sulphates are quite stable in the dark, but on exposure to light rapidly decompose. In aqueous solution, a small amount of bromine is eliminated, and the 3 : 5-dibromocresol, which separates during the change, is discoloured by the products of decomposition of the quinonediazide. Quantitative experiments have shown, however, that only 10 per cent. of the diazonium salt undergoes the quinonediazide decomposition, the remaining 90 per cent. being converted into cresol. If the decomposition is carried out in 15 per cent. sulphuric acid solution, no bromine is eliminated, and the cresol separates in almost pure, colourless needles.

The cresols can easily be isolated from the product of the action of light by distilling in steam. 3 : 5-Dibromo-*o*-cresol crystallised in long needles melting at 55°:

0·1372 gave 0·1932 AgBr. Br = 59·93.

$C_7H_6OBr_2$ requires Br = 60·12 per cent.

3 : 5-Dibromo-*p*-cresol was obtained in needles melting at 43—44°:

0·1506 gave 0·2123 AgBr. Br = 59·98 per cent.

When dilute (1 per cent.) aqueous solutions of the sulphates are heated at 100°, rapid decomposition ensues; about 70 per cent. of the total nitrogen in the diazo-compound is given off as gas. A dark brown, amorphous solid separated from which no cresol could be isolated; the filtrate was quite colourless and free from both unchanged diazonium compound or quinonediazide, but a trace of bromine was present.

The dibromodiazotoluenes differ from tribromodiazobenzene in that they readily yield the corresponding cresols when they are heated in solution in 63 per cent. sulphuric acid. Decomposition is very rapid, and a crystalline substance distils over, which is mainly the cresol.

Solutions of the sodium dibromotoluenediazotates can be easily prepared, and accordingly offer an excellent means of demonstrating the stability of these substances to light. After three days' exposure of the sodium derivative of dibromo-*o*-diazotoluene in 1 per cent. aqueous solution, the liquid was still quite colourless; no measurable amount of gas had been evolved.

The authors are indebted to the Chemical Society and to the British Association for the Grants which have largely defrayed the cost of these researches. They wish to take this opportunity of expressing their thanks to these Societies.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

V.—*On the More Exact Determination of the Densities of Crystals.*

By THE EARL OF BERKELEY.

THIS communication was read at the meeting of the British Association at Bristol in 1898. It has not hitherto been published as it was part of a somewhat lengthy research on the molecular volumes of crystals. The appearance of Messrs. Barlow and Pope's recent paper (Trans., 1906, **89**, 1675) has so illuminated the subject, that it is not considered necessary to pursue the matter any further.

A comparison of the several values obtained by different observers, for the density of one and the same salt, shows variations which in some cases amount to 10 per cent. As the density is supposed to be independent of the way in which the crystals have been produced, these discordant results must be ascribed to errors of observation.

Of these errors the following seem to be the most important.

(1) Errors in the operation of determining the density.

(2) Errors caused by air adhering to the crystals.

(3) Errors due to the hygroscopic nature of the salts.

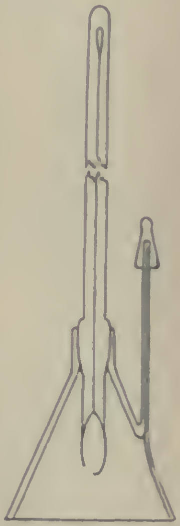
(4) Errors induced by the mother liquor occluded in the crystals.

In this paper I propose to describe the means whereby the amount of error due to the first three causes have, I believe, been reduced.

(1) *Operation of Determining the Density.*—Two similar conical pyknometers (Fig. 1), of about 7 c.c. capacity, were made by Mr. Müller from Jena thermometer glass. These are fitted with carefully ground thermometer stoppers and the thermometers are graduated in tenths of a degree such that the hundredth of a degree can be estimated. The thermometers were standardised at Kew. The side capillaries are graduated in millimetres and were calibrated by running weighed mercury threads along the bores and reading their lengths.

The capacity (7 c.c.) was chosen as being sufficiently great to keep down errors of weighing and of manipulation. The greater the capacity of the pyknometer the thicker the walls; consequently it will take more than proportionately longer for the larger quantity of liquid to attain a constant temperature when in the balance case. Also a greater quantity of salt will be required to keep the proportion of salt to liquid the same, and hence the more difficult it will be to dry and to free from adhering air. One of the pyknometers was used throughout the weighings as a counterpoise, and to obtain the most accurate results I found it essential that the surface of each pyknometer should be similarly treated; if, for instance, the pyknometer itself had been filled with carbon tetrachloride and its surface wetted with that liquid, the surface of the counterpoise should also be wetted with the same liquid and both similarly dried before weighing.

FIG. 1.



The pyknometers, after steaming for twenty minutes, were heated to 130° and cooled; this heating and cooling was repeated about fifty times so as to obtain, as far as possible, a constant state of molecular aggregation in the glass.

(*a*) The capacity of the pyknometer was then determined. It was filled with distilled water and placed in a small desiccator connected to a Sprengel pump. Vigorous boiling, which was continued for three-quarters of an hour, was promoted by tapping the bottom of the desiccator. The pyknometer was then placed on the pan of an ordinary spring balance and the stopper inserted and pressed home, the reading of the balance index being noted so that in future the stopper could be pressed home with the same pressure; the presumption is that with the same pressure and the same orientation of stopper to neck, the former will go home to the same extent. It is well, however, to check this assumption by redetermining the capacity; for after much use the stopper is ground further into the neck, especially if powdered minerals have been used.

After the pyknometer and its counterpoise have been wiped dry, they are placed on the pans of the balance, and when the level of the liquid in the capillary has, in consequence of evaporation round the neck, fallen below the highest graduation, the weight is determined, and at the same time the level in the capillary and the temperature of the liquid are noted; care, however, should be taken that the temperature is fairly constant. From these data the capacity of the pyknometer is calculated in the usual way, all weights being corrected for displaced air.

The following are the values obtained for this capacity, reduced to the zero mark of the capillary:

Temp.	Capacity.	Temp.	Capacity.
14·90°	7·15303 c.c.	15·27°	7·15315 c.c.
14·95	7·15322 ,,	15·60	7·15298 ,,
14·95	7·15305 ,,	15·52	7·15316 ,, *
14·97	7·15293 ,,	15·96	7·15311 ,, *

The greatest difference between any two observations is 0·00029 c.c. and this corresponds to an error of 0·004 per cent.

The mean of these numbers was taken as the capacity at the mean temperature, and the capacity at any other temperature was calculated from the known cubical expansion of the Jena glass.

(*b*) The liquid used for determining the volume occupied by the crystals was carbon tetrachloride. It was purchased from Messrs. Kahlbaum and redistilled at constant temperature after digesting with fused calcium chloride for several weeks. Both during the distillation and when drawing off the liquid for use, the access of moist air was prevented by means of calcium chloride tubes.

The density of the carbon tetrachloride was found to be the same at the end of a year as it was shortly after distillation. The pyknometer is filled with air-free carbon tetrachloride in a manner similar to that already described, and then wiped dry as in the case of water.

Owing to the high coefficient of expansion of the liquid, it is important that the pyknometer thermometer should register the true temperature of the liquid and glass. A double-walled glass case surrounding the balance case was found insufficient to secure a steady temperature, and eventually a zinc tank filled with water and placed over and round three sides of the balance, whilst the heat of the observer was cut off on the fourth side by a glass trough filled with water, was substituted and found effectual. By this means, in about one and a half hours, after placing the pyknometer on the balance, the thermometer does not change by more than 0·01° in fifteen minutes.

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* These observations were obtained after an interval of some weeks.

The following table gives the densities of the carbon tetrachloride used, and for comparison, those calculated from Prof. Thorpe's results (Trans., 1880, **37**, 199):

Temp.	Density.		Diff.
	Self.	Thorpe.	
16·44°	1·60133	1·59980	0·00153
16·33	1·60157	1·60003	0·00154
16·17	1·60189	1·60033	0·00156
15·55	1·60310	1·60155	0·00155
14·88°	1·60438	1·60286	0·00152
14·68	1·60475	1·60324	0·00151
13·94	1·60620	1·60467	0·00154

Thinking that the somewhat large differences between our values might be caused by dissolved air, I determined the density of my unboiled carbon tetrachloride with the following results:

Temp.	Self.	Thorpe.	Diff.
15·47°	1·60291	1·60171	0·00121
15·35	1·60320	1·60195	0·00125

To show the effect of the rate of change of temperature when the pyknometers are on the balance pans, I append the following:

Temp.	Rate of change.	Density.		Diff.
		Self.	Thorpe.	
15·67°	0·04° in 20 minutes (falling)	1·60274	1·60132	0·00142
14·34	0·02 ,, 10 ,, ,,	1·60534	1·60390	0·00144
17·67	0·03 ,, 20 ,, ,,	1·59904	1·59741	0·00163
14·04	0·02 ,, 15 ,, (rising)	1·60584	1·60448	0·00136
16·92	0·02 ,, 20 ,, ,,	1·60052	1·59887	0·00167
16·42	0·04 ,, 20 ,, ,,	1·60144	1·59984	0·00160

(*c*) To determine the density of the crystals, the pyknometer, containing a known weight of salt, is placed in the "bulb desiccator" (shown in Fig. 2), the bulb of which has previously been half-filled with carbon tetrachloride. The liquid is then caused to boil by exhausting through *A*, and warming and tapping the bottom of the bulb. Tap *A* is then closed, and the exhaustion continued through *B* for at least three-quarters of an hour, the bottom of the desiccator being vigorously tapped at intervals so that the vapour of the liquid may penetrate among the powdered crystals and thus sweep out the air. The apparatus is then disconnected from the pump and while still vacuous is tilted so that the liquid in the bulb flows down the fine capillary, *C*, into the pyknometer. The pyknometer is then weighed as already detailed.

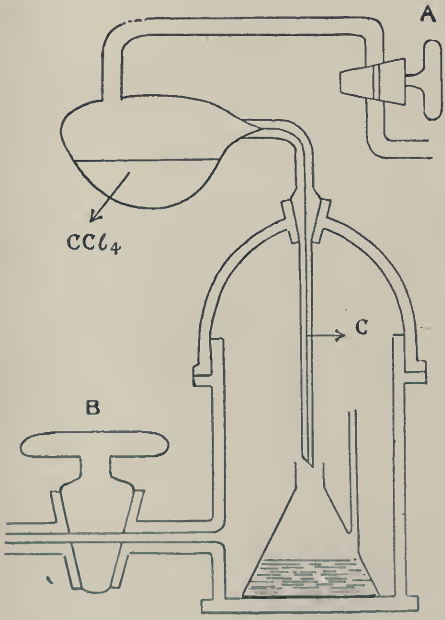
The following results were obtained for the density of powdered and ignited quartz :

Density of Quartz.

Observed in water.		Observed in carbon tetrachloride.		
			Density.	
Temp.	Density.	Temp.		
21·95°	2·6484	21·14°	2·6486	2·6486
21·75	2·6487	21·07	2·6480	2·6480
21·52	2·6487	20·18	2·6483	2·6482
21·48	2·6487	19·99	2·6485	2·6484
21·24	2·6486	18·85	2·6483	2·6480
		18·24	2·6489	2·6486

In the last column, the density observed in carbon tetrachloride is corrected to 21° by the use of Fizeau's coefficient of expansion of quartz. The greatest difference between any two of these is 0·0007, which corresponds to a maximum error of 0·02 per cent.

Fig. 2.



It was considered possible that there might be some difference in the densities of large and small fragments of the same substance. A clear specimen of barytes was selected, coarsely powdered, and then sifted through sieves of different mesh. The density of the fragments retained by the finest mesh, the openings of which average 0·36 by 0·33 mm., was compared with that of the fragments retained by the medium mesh (0·59 by 0·54 mm.). The barytes fragments were heated to 200° and cooled over sulphuric acid before each observation. The results are as follows :

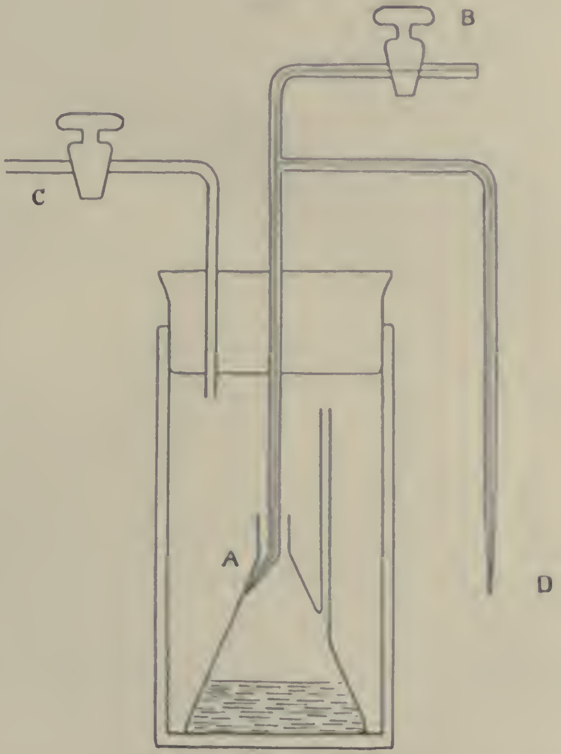
Density of Barytes.

Small fragments.		Large fragments.	
Temp.	Density.	Temp.	Density.
* 15·76°	4·4700	* 16·46°	4·4702
* 15·96	4·4698	* 15·05	4·4707
16·67	4·4696	17·35	4·4701
16·75	4·4702	17·06	4·4697
16·07	4·4703		

The observations marked (*) were obtained with fragments immersed in water, the remainder in carbon tetrachloride. The greatest difference between any two observations is 0·0011, which corresponds to a maximum error of 0·025 per cent. It will be noticed that there seems to be no difference between the two sets of densities.

(2) *Air Held by the Crystals.*—In section (*c*) I have already described the method whereby it was hoped that the air difficulty had been overcome. It is evident that the shape of the pyknometer lends itself to this method, for the salt, while conserving the same relative proportion of salt to liquid, can lie in a thinner stratum than in either a cylindrical or globular form of pyknometer.

FIG. 3.



The ordinary method of covering the salt with the liquid and boiling in a vacuum leads to loss of salt through spirting, and also to the adhesion of small particles to the inside of the neck which prevents the stopper from going right home.* The method of boiling has, however, to be employed in the case of hygroscopic salts.

(3) *Moisture Retained by the Crystal Faces.*—The apparatus shown in Fig. 3 was found satisfactory. The crystals are placed in the pyknometer, which is brought into *A* and a current of dry air passed over them, entering by *B* and leaving by *C* to go through a tared U-tube containing phosphorus pentoxide. The lower part of the desiccator is heated in an air-oven to whatever temperature is necessary to expel the moisture, and the air current is stopped when the phosphorus pentoxide tube reaches a constant weight. The whole apparatus is then exhausted, and the end of the capillary tube, *D*, broken under carbon tetrachloride. When the crystals have been covered to a depth of about 1 centimetre, the pyknometer and its contents are transferred to the "bulb desiccator," and the liquid covering the salt is boiled for about three-quarters of an hour; the pyknometer is then filled and weighed as before.

The weight of crystals introduced can be found by evaporating the carbon tetrachloride after the density has been determined.

This method was tested on potassium carbonate with the following results:

Density of Potassium Carbonate.

Temp.	Density.	Temp.	Density.
16·20°	2·3320	16·13°	2·3314
16·14	2·3322	17·00	2·3312

The maximum error is 0·04 per cent.

(4) *Mother Liquor in the Crystals.*—No general method of overcoming this source of error was found. Some substances give the same density when obtained under conditions which differ fairly widely, but others, such as potassium chloride, even when crystallised from a solution which was kept at a constant temperature and continuously stirred, give successive crops which differ markedly in their density.

The greater part of this investigation was carried out at the Christ Church Laboratory, Oxford; I am glad to have this opportunity of thanking Mr. A. Vernon Harcourt for his kind permission to use the resources of this laboratory.

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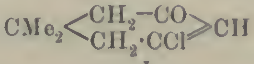
* A useful precaution to take is to note the rate at which the carbon tetrachloride evaporates normally (loss of weight) when on the balance; the presence of particles in the neck will be indicated by an increase in the rate.

VI.—*Action of Reducing Agents on 5-Chloro-3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene.*

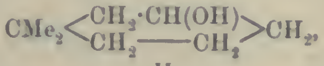
By Arthur William Crossley and Nora Renouf, Salters' Research Fellow.

Some little time since (Trans., 1905, **87**, 1487), the authors described the action of sodium in moist ethereal solution on 5-chloro-3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene (I) and showed that the main product,



$$CMe_2{<}\substack{CH_2-CO\\ CH_2\cdot CCl}{\geqslant}CH$$

I.

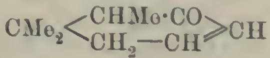


$$CMe_2{<}\substack{CH_2\cdot CH(OH)\\ CH_2-\!\!-\!\!-CH_2}{>}CH_2,$$

II.

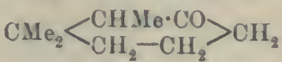
of the reaction was 3-hydroxy-1 : 1-dimethylhexahydrobenzene (II), which may be described as the limit reduction product of the chloroketone. The main object of the present investigation was to find reducing agents, less powerful than sodium in moist ethereal solution, which would be discriminating in their action; so that it might be possible to prepare from chloroketodimethyltetrahydrobenzene, first, a ketodimethyltetrahydrobenzene, differing from the former only in that chlorine would be replaced by hydrogen, and secondly, the corresponding ketodimethylhexahydrobenzene.

Chloroketodimethyltetrahydrobenzene is readily prepared from dimethyldihydroresorcin (see page 69) by the action of phosphorus trichloride, the yield being 75 per cent. of the theoretical amount; and as other substituted dihydroresorcins give equally good yields of the corresponding chloroketones, it is evident that if the above-mentioned reactions could be realised, they would furnish very ready methods for preparing substituted ketotetrahydro- and ketohexahydrobenzenes, which substances, especially the former, are not easy to obtain by the present known methods. Complete success has attended the experiments, and further work is in progress with the object of proving that the reactions are general ones. Particular attention is being paid to the ketones (III and IV) derivable from trimethyldihydroresorcin, on account of the great similarity in the



$$CMe_2{<}\substack{CHMe\cdot CO\\ CH_2-CH}{\geqslant}CH$$

III.



$$CMe_2{<}\substack{CHMe\cdot CO\\ CH_2-CH_2}{>}CH_2$$

IV.

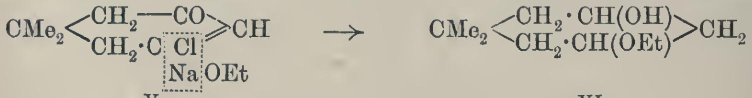
groupings which they contain when compared with those of camphor.

The action of sodium in moist ethereal solution on chloroketodimethyltetrahydrobenzene has been further investigated, and it has been proved that the addition of a small quantity of alcohol to the ether has a beneficial effect, considerably increasing the yield of hydroxydimethylhexahydrobenzene and rendering it much easier to remove the chlorine completely from the chloroketone. Further, several interesting substances have been isolated from the resinous by-product (Trans., 1905, 87, 1494) which are dicyclic in composition. Similar resins have been encountered in all the reducing actions which have been tried, and as the constitutions of the substances derived from them have close relationship with one another, it will be most convenient to describe first the single nucleus compounds produced in these reactions and afterwards the dicyclic derivatives.

Single Nucleus Compounds.

Having found that alcohol had such a decided influence in the reaction between chloroketodimethyltetrahydrobenzene and sodium in moist ethereal solution, it was thought advisable to try the action of sodium in absolute alcoholic solution. The reaction proceeded, however, in an unexpected direction, and though giving an interesting body from quite another point of view, did not further the object of the present inquiry. It demonstrated the fact that the chlorine atom in chloroketodimethyltetrahydrobenzene is very reactive, a fact which greatly enhances the possibilities of the use of this and similar chloroketones for synthetical purposes.

The reaction gives rise to small quantities of hydroxydimethylhexahydrobenzene (II), but principally 3-*hydroxy*-5-*ethoxy*-1 : 1-*dimethylhexahydrobenzene* (VI). Evidently the sodium ethoxide formed

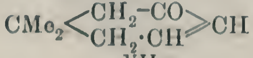


$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2—CO}\\ \mathrm{CH_2\cdot C\,\boxed{Cl}}\\ \quad\ \ \mathrm{\boxed{Na}\,OEt}\end{matrix}\!\!>\mathrm{CH} \longrightarrow \mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2\cdot CH(OH)}\\ \mathrm{CH_2\cdot CH(OEt)}\end{matrix}>\mathrm{CH_2}$$

V. VI.

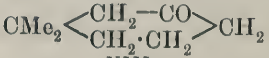
in the first stages of the reduction reacts with the chlorine atom of the chloroketone to give the substance represented by formula V, which is then further reduced to the corresponding saturated compound. The constitution of the latter is proved by analysis and by the facts that a Zeisel determination shows it to contain an ethoxy-group, and that, when treated with acetyl- or benzoyl chlorides, it yields acetyl- or benzoyl-derivatives respectively.

The next reducing agent employed was zinc dust in aqueous alcoholic solution, which, as previously shown (Trans., 1905, 87, 1497; 1906, 89, 43), readily replaces halogen by hydrogen in saturated hydroaromatic substances, but in the present instance its action is too powerful, as it gives a mixture of the ketones represented by formulæ VII and VIII, containing approximately 30 per cent. of the latter. However, 3-*keto*-1 : 1-*dimethyl*-Δ^4-*tetrahydrobenzene* (VII) may be obtained quite pure by replacing zinc dust by



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2—CO}\\ \mathrm{CH_2\cdot CH}\end{matrix}\geqslant\mathrm{CH}$$

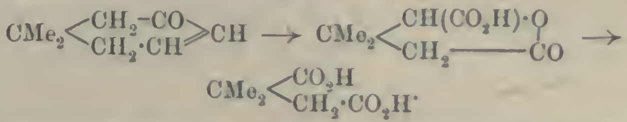
VII.



$$\mathrm{CMe_2}<\begin{matrix}\mathrm{CH_2—CO}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2}$$

VIII.

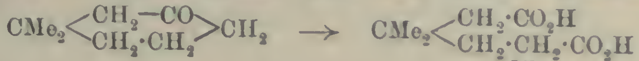
zinc filings, either in the cold or on heating, or by using the zinc copper couple. It is a colourless liquid boiling at 88·5° at 32 mm., and its ketonic nature is proved by the fact that it gives a semicarbazone and an oxime. When oxidised with potassium permanganate in the cold, it yields *as*-dimethylsuccinic acid and the lactone of α-hydroxy-$\beta\beta$-dimethylglutaric acid:



$$\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH}\end{matrix}{\geqslant}\mathrm{CH} \longrightarrow \mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH(CO_2H){\cdot}O}\\ \mathrm{CH_2 \text{———} CO}\end{matrix} \longrightarrow \mathrm{CMe_2}{<}\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CH_2{\cdot}CO_2H}\end{matrix}$$

These products were also obtained by the oxidation of chloroketodimethyltetrahydrobenzene (Trans., 1903, **83**, 119) together with $\beta\beta$-dimethylglutaric acid. The production of the lactone of α-hydroxy-$\beta\beta$-dimethylglutaric acid proves quite definitely the constitution of the ketone, although its formation cannot be explained on the lines suggested in the case of the chloroketone. From the present instance, it would appear that the production of this lactone must be regarded as almost certain in any oxidation where the degradation of a ring is concerned and which might reasonably be expected to yield $\beta\beta$-dimethylglutaric acid.

3-*Keto*-1 : 1-*dimethylhexahydrobenzene* (VIII) may be produced from chloroketodimethyltetrahydrobenzene by heating it with zinc dust in glacial or dilute acetic acid solution. It is a colourless liquid boiling about 10° lower (75·5° at 25 mm.) than the corresponding unsaturated ketone. It forms an oxime and a semicarbazone, and when oxidised with potassium permanganate gives only $\beta\beta$-dimethyladipic acid



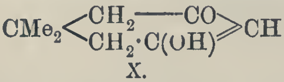
$$\mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH_2{-}CO}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{CH_2} \longrightarrow \mathrm{CMe_2}{<}\begin{matrix}\mathrm{CH_2{\cdot}CO_2H}\\ \mathrm{CH_2{\cdot}CH_2{\cdot}CO_2H}\end{matrix}$$

IX.

(IX), a fact which proves its constitution beyond doubt.

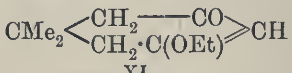
One slight difference is observable in the specimens of the ketone, according as to whether glacial or dilute acetic acid is employed in their preparation. In the latter case, the ketone gives a faint colour reaction with concentrated sulphuric acid, indicating the presence of traces of ketodimethyltetrahydrobenzene, which is not, however, produced in sufficient amount to influence the analysis of the substance, and which can be completely and easily removed by treatment with a small quantity of dilute potassium permanganate solution in the cold. The choice between dilute and glacial acetic acid would be influenced according as to whether the solid by-product (m. p. 148°, see page 82) was required for investigation, as a larger proportion of the latter substance is obtained when dilute acetic acid is employed, although the yield of ketodimethylhexahydrobenzene is not so good as when glacial acetic acid is used.

Other reducing agents investigated were zinc dust in strongly alkaline solution, also zinc dust and hydrogen chloride in alcoholic solution. In the former case, the hydrolytic action of the potassium hydroxide overshadows the reducing action of the zinc, with the result that the only product isolated was dimethyldihydroresorcin (X). In the latter case, a mixture of ketodimethyltetrahydrobenzene and ketodimethylhexahydrobenzene was obtained, together with dimethyldihydroresorcin and its ethyl ether (XI) (Trans., 1899, **75**, 775).



$$\mathrm{CMe_2}\left<\begin{array}{l}\mathrm{CH_2}\text{——}\mathrm{CO}\\ \mathrm{CH_2\cdot C(OH)}\end{array}\right>\mathrm{CH}$$

X.



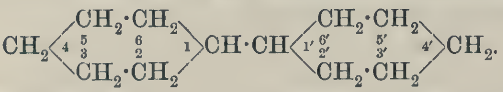
$$\mathrm{CMe_2}\left<\begin{array}{l}\mathrm{CH_2}\text{——}\mathrm{CO}\\ \mathrm{CH_2\cdot C(OEt)}\end{array}\right>\mathrm{CH}$$

XI.

Here again hydrolysis must first take place, giving rise to dimethyldihydroresorcin, which is then esterified by the alcoholic hydrogen chloride.

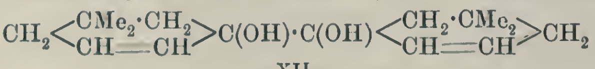
Dicyclic Compounds.

The compounds of this nature met with are all derivatives of a substance formed theoretically by the removal of one hydrogen atom from each of two hexahydrobenzene rings, with consequent production of dicyclic derivatives. It has been decided to refer to this substance as di*cyclo*hexane, and to indicate the positions of the various substituting groups by adopting the following scheme of numbering:



$$\mathrm{CH_2}\left<{}^{4}\begin{array}{c}\mathrm{CH_2\cdot CH_2}\\ {}^{5}_{3}\qquad{}^{6}_{2}\\ \mathrm{CH_2\cdot CH_2}\end{array}{}^{1}\right>\mathrm{CH\cdot CH}\left<{}^{1'}\begin{array}{c}\mathrm{CH_2\cdot CH_2}\\ {}^{6'}_{2'}\qquad{}^{5'}_{3'}\\ \mathrm{CH_2\cdot CH_2}\end{array}{}^{4'}\right>\mathrm{CH_2}.$$

When zinc dust acts on chloroketodimethyltetrahydrobenzene in aqueous solution, there is obtained a mixture of ketodimethyltetrahydrobenzene and ketodimethylhexahydrobenzene (VII and VIII), in which the former largely predominates. If this mixture of ketones is again treated several times with zinc dust, it is possible to isolate pure ketodimethylhexahydrobenzene and a semi-solid mass from which a crystalline product has been separated, melting at 148°, and having the composition $C_{16}H_{26}O_2$, and which is believed to be 1 : 1′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyl*-$\Delta^{2:2'}$-*di*cyclo*hexene* (XII). Another possibility for a substance of this composition would be that represented by formula XIII, which could be produced from chloroketodimethyltetrahydrobenzene * by the zinc coupling two molecules together and then partially reducing the unsaturated diketone so formed.



$$\mathrm{CH_2}\left<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CH{=\!=}CH}\end{array}\right>\mathrm{C(OH)\cdot C(OH)}\left<\begin{array}{l}\mathrm{CH_2\cdot CMe_2}\\ \mathrm{CH{=\!=}CH}\end{array}\right>\mathrm{CH_2}$$

XII.

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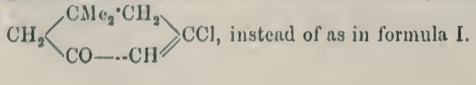
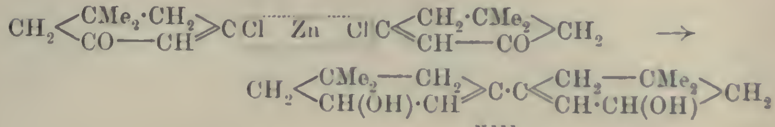
* To make the formulæ of these dicyclic compounds strictly comparable with those of the single nucleus derivatives, chloroketodimethyltetrahydrobenzene should be written



$$\mathrm{CH_2}\left<\begin{array}{l}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CO{-\!-}CH}\end{array}\right>\mathrm{CCl},$$

instead of as in formula I.

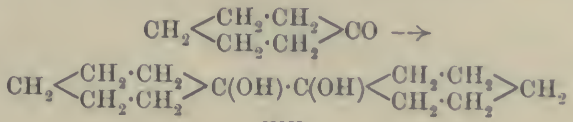


$$CH_2<\begin{matrix}CMe_2\cdot CH_2\\ CO{-\!-}CH\end{matrix}\geqslant C\,Cl \cdots Zn \cdots Cl\,C\leqslant\begin{matrix}CH_2\cdot CMe_2\\ CH{-\!-}CO\end{matrix}>CH_2 \longrightarrow$$

$$CH_2<\begin{matrix}CMe_2{-\!-}CH_2\\ CH(OH)\cdot CH\end{matrix}\geqslant C\cdot C\leqslant\begin{matrix}CH_2{-\!-}CMe_2\\ CH\cdot CH(OH)\end{matrix}>CH_2$$

XIII.

Such a presumption is, however, at once rendered impossible when it is remembered that the substance is not formed directly from the chloroketone but from the halogen-free mixture of ketones, obtained by the initial action of zinc dust on chloroketodimethyltetrahydrobenzene. There can be therefore no doubt in this case that the substance $C_{16}H_{26}O_2$ owes its origin to pinacone formation, an exactly analogous case having been observed in the reduction of ketohexahydrobenzene (Trans., 1904, **85**, 1415), where considerable amounts of 1 : 1-dihydroxydi*cyclo*hexane (XIV), (ketohexamethylene pinacone) were formed.

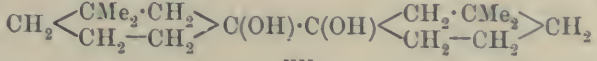


$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CO \longrightarrow$$

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$$

XIV.

Moreover, the behaviour of dihydroxytetramethyldi*cyclo*hexene is quite in accord with that of a substance having formula XII, for it does not give a colour reaction with concentrated sulphuric acid, nor can it be acetylated or benzoylated under the conditions employed. Further, its unsaturated nature is proved by the fact that it readily absorbs bromine with elimination of hydrogen bromide and formation of what is believed to be a tribromoanhydride, but the exact constitution of this compound is at present doubtful. Also, when treated with sodium in moist ethereal solution, it absorbs four atoms of hydrogen to give 1 : 1′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldi*cyclo*hexane* (XV). Here again this saturated pinacone does not give a colour



$$CH_2<\begin{matrix}CMe_2\cdot CH_2\\ CH_2{-}CH_2\end{matrix}>C(OH)\cdot C(OH)<\begin{matrix}CH_2\cdot CMe_2\\ CH_2{-}CH_2\end{matrix}>CH_2$$

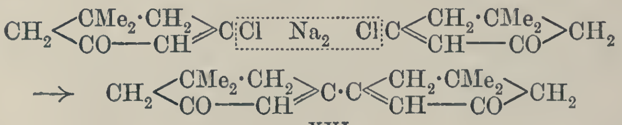
XV.

reaction with concentrated sulphuric acid, but it is surprising to find that it is acetylated or benzoylated very readily. No explanation of this fact can be offered on the present occasion, but it is hoped that, as the work proceeds, other similarly constituted pinacones will be encountered, when the matter will receive further attention.

It may at first sight appear strange that zinc dust in aqueous alcohol is a reagent sufficiently strong to reduce the double bond in ketodimethyltetrahydrobenzene, giving ketodimethylhexahydrobenzene, and also strong enough to form dihydroxytetramethyldi*cyclo*hexene from ketodimethyltetrahydrobenzene, yet is not strong enough to reduce the di*cyclo*hexene compound to the corresponding saturated derivative. But such is undoubtedly the case, for on boiling an aqueous alcoholic solution of dihydroxytetramethyldi*cyclo*hexene with zinc dust for twelve hours, no trace of any reduction having taken place could be detected and only the unsaturated di*cyclo*hexene compound was recovered.

Moreover, the reduction of ketodimethyltetrahydrobenzene to ketodimethylhexahydrobenzene by zinc dust in aqueous alcohol proceeds extremely slowly, and from the experiments described on page 75 it can only be concluded that, under the influence of this particular reducing agent, the unsaturated pinacone is more easily formed than ketodimethylhexahydrobenzene.

In the preparation of hydroxydimethylhexahydrobenzene considerable difficulty was experienced at one time (see page 70) in obtaining the product free from halogen, and on examining the resinous by-product formed under these conditions, two solid substances were separated from it melting respectively at 178° and 173—174°. The former of these has the composition $C_{16}H_{22}O_2$ and is apparently 3 : 3′-*diketo*-5 : 5 : 5′ : 5′-*tetramethyl*-$\Delta^{1:1'}$-*di*cyclo*hexene* (XVI), formed



$$CH_2{<}\begin{matrix}CMe_2{\cdot}CH_2\\CO{-\!\!-}CH\end{matrix}{>}C\boxed{Cl\quad Na_2\quad Cl}C{<}\begin{matrix}CH_2{\cdot}CMe_2\\CH{-\!\!-}CO\end{matrix}{>}CH_2$$

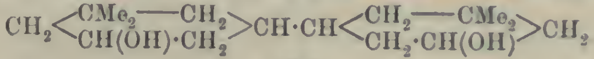
$$\longrightarrow\quad CH_2{<}\begin{matrix}CMe_2{\cdot}CH_2\\CO{-\!\!-}CH\end{matrix}{>}C{\cdot}C{<}\begin{matrix}CH_2{\cdot}CMe_2\\CH{-\!\!-}CO\end{matrix}{>}CH_2$$

XVI.

by the direct coupling of 2 molecules of chloroketodimethyltetrahydrobenzene by the sodium. It is highly coloured (yellow), gives a brick-red disemicarbazone, thus proving its diketonic nature, and is unsaturated as shown by its ready absorption of bromine. It could not be detected in the resin formed when alcohol was added to the ether used in the reduction of chloroketodimethyltetrahydrobenzene, but much larger quantities of the second substance melting at 173—174° and also another compound melting sharply at 212° were isolated. The latter proved to be identical with 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane (see page 67).

For a long time the substance melting at 173—174° was thought to be homogeneous, as it gave on analysis numbers agreeing with the formula $C_{16}H_{30}O_2$, nor was its melting point altered by many recrystallisations, and moreover it sublimed in needles which melted at 171—172°. Nevertheless it was found to be a mixture, for on acetylation it gave two diacetyl derivatives melting at 130° and 68°, and on benzoylation, two dibenzoyl derivatives melting at 199° and 134°. The former of the diacetyl and dibenzoyl compounds (m. p. 130° and 199°) proved to be diacetyl- and dibenzoyl-1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane, which substance they yielded on hydrolysis.

The above-mentioned derivatives melting at 68° and 134° were separately hydrolysed with alcoholic potassium hydroxide, when they each gave a substance, $C_{16}H_{30}O_2$, melting at 183°, which is believed to be 3 : 3′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldicyclohexane* (XVII). It



$$CH_2<\begin{matrix}CMe_2—CH_2\\CH(OH)\cdot CH_2\end{matrix}>CH\cdot CH<\begin{matrix}CH_2—CMe_2\\CH_2\cdot CH(OH)\end{matrix}>CH_2$$

XVII.

is readily acetylated and benzoylated, and, unlike the unsaturated or saturated pinacones, gives a decided colour reaction with sulphuric acid. Its formation would be due to the further reduction of diketotetramethyldi*cyclo*hexene (XVI), although, unfortunately, sufficient of the latter material could not be isolated to try the action of reducing agents upon it.

The substance melting at 173—174° is therefore a mixture of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane (XV) and 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane (XVII), in the approximate proportion of one part of the former to three parts of the latter, and it has been ascertained that a mixture of these substances in these proportions melts at 173—174° and sublimes in needles melting at 171—172°.

It would appear, therefore, that in the reduction of chloroketodimethyltetrahydrobenzene with sodium in moist ethereal solution, dicyclic compounds are formed both by the process of pinacone formation and by the coupling reaction of the sodium. Further, when the reduction is inefficient, there are formed 3 : 3′-diketo-5 : 5 : 5′ : 5′-tetramethyl-$\Delta^{1:1'}$-di*cyclo*hexene (XVI) and small amounts of 1 : 1′-dihydroxy- and 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane; but when the reduction is facilitated by addition of alcohol to the ether, the first of these three substances cannot be isolated, as it is further reduced to 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane.

EXPERIMENTAL.

Chloroketodimethyltetrahydrobenzene was prepared as already described (Trans., 1903, 83, 117), except that the heating with phosphorus trichloride was continued for three hours instead of two and a half hours. Moreover, after working up the product, the alkaline washings should be acidified with sulphuric acid, when a considerable amount of solid matter separates, consisting largely of unaltered dimethyldihydroresorcin, and if this is again treated with phosphorus trichloride, the yield of chloroketodimethyltetrahydrobenzene may be increased to 75 per cent. (instead of 66 per cent.) of the theoretical amount.

The boiling point of the ketone, after repeated distillation, is somewhat lower than previously stated (*loc. cit.*), namely 99° at 20 mm., and its great stability is a point worth calling attention to. On exposure to air and light, it darkens in colour and deposits crystals of dimethyldihydroresorcin hydrochloride, but if protected from air and light it may be kept for an almost indefinite period. A specimen which had been bottled in this way for three years was found to be faintly yellow, and contained 1 gram of crystalline dimethyldihydroresorcin hydrochloride. After filtration, there remained 37 grams of a liquid, which were dissolved in ether, the ethereal solution washed with potassium hydroxide solution, then with water, dried over calcium chloride, and the ether evaporated. On distilling the residue in a vacuum, 36 grams passed over quite constantly with the above-mentioned boiling point of chloroketodimethyltetrahydrobenzene.

Reduction of Chloroketodimethyltetrahydrobenzene.

I. *With Sodium in moist Ethereal Solution.*

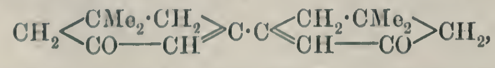
The main product obtained by this reaction is 3-hydroxy-1 : 1-dimethylhexahydrobenzene, which has already been described in detail (Trans., 1905, **87**, 1494). Considerable difficulty was experienced at one time in obtaining this substance free from chlorine, until it was realised that in the original preparation the ether employed had not been washed with water to remove alcohol. Further experiments have shown that, if the amounts of materials as already stated be used, with the addition of 20 c.c. of absolute alcohol to the ether, the product of the reaction is always free from halogen. Moreover, the yield of hydroxydimethylhexahydrobenzene is thereby increased to 60 per cent. of the theoretical amount.

During the preparation resinous matter is always formed, varying in amount from 25 to 30 grams from 100 grams of chloroketodimethyltetrahydrobenzene. The material obtained when difficulty was experienced in producing hydroxydimethylhexahydrobenzene free from halogen was a thick, red jelly, which was dissolved in the smallest possible amount of light petroleum (b. p. 80—100°) and allowed to stand. A viscid, yellow solid gradually separated (2·3 grams from 75 grams of the jelly), which was repeatedly crystallised from methyl alcohol:

0·1078 gave 0·3076 CO_2 and 0·0871 H_2O. C = 77·82; H = 8·97.

$C_{16}H_{22}O_2$ requires C = 78·04; H = 8·94 per cent.

3 : 3′-*Diketo*-5 : 5 : 5′ : 5′-*tetramethyl*-$\Delta^{1:1'}$-*di*cyclo*hexene*,



$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CMe_2\cdot CH_2}\\ \mathrm{CO{-}{-}CH}\end{matrix}{>}\mathrm{C\cdot C}{<}\begin{matrix}\mathrm{CH_2\cdot CMe_2}\\ \mathrm{CH{-}{-}CO}\end{matrix}{>}\mathrm{CH_2},$$

is readily soluble in the cold in chloroform or benzene, and crystallises from light petroleum (b. p. 80—100°), ethyl acetate, or methyl alcohol in deep yellow needles melting at 178°. When a solution of bromine in chloroform was added to a solution of the ketone in the same solvent and the whole slightly warmed, the bromine disappeared and hydrogen bromide was evolved. On evaporating the solvent, a white solid remained, which crystallised from absolute alcohol and melted at 165° with evolution of gas, but the amount of material was too small to permit of the reaction being thoroughly investigated.

The *disemicarbazone* was prepared in the usual manner and separated from the alcoholic solution as a micro-crystalline, brick-red powder melting about 273° with decomposition. On account of its insolubility in the ordinary organic solvents, it was not found possible to purify it by crystallisation, and it was therefore analysed after being well washed with absolute alcohol:

Found, N = 23·38. $C_{18}H_{28}O_2N_6$ requires N = 23·33 per cent.

The light petroleum solution of the original red jelly gave a second small crop of solid matter, which was white, and consisted of 1 : 1′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldi*cyclo*hexane*, melting at 212°, (see page 77) and of 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane melting at 183° (see page 72).

When the reduction of chloroketodimethyltetrahydrobenzene by sodium in moist ethereal solution is carried out as described on page 70, the by-product sets to a hard, transparent, reddish-yellow resin. This was dissolved in benzene, light petroleum (b. p. 40—60°) added, and the whole allowed to stand, when solid matter separated, which was filtered and well washed with light petroleum. By treatment in this manner, 80 grams of resin yielded 15 grams of a white solid, from which two substances of constant melting point (*A* and *B*) were separated by means of a somewhat tedious process of fractional extraction with ethyl acetate and repeated crystallisation from the same solvent.

The smaller fraction *A*, weighing 2·2 grams, crystallised from ethyl acetate in oblique, square plates melting at 212°, and was proved by analysis and the preparation from it of acetyl and benzoyl derivatives, to be identical with 1 : 1′-*dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldi*cyclo*hexane*, described on page 77.

The larger fraction, *B* (5·1 grams), was analysed with the following results:

0·1275 gave 0·3529 CO_2 and 0·1353 H_2O. C = 75·48; H = 11·79.
$C_{16}H_{30}O_2$ requires C = 75·59; H = 11·81 per cent.

This substance crystallised from ethyl acetate in radiating clusters of transparent, leaf-like aggregates melting at 173—174°,* nor was this melting point altered by repeated crystallisation. On account of this fact, and also because it sublimed unchanged (m. p. 171—172°) in long, silky needles, it was for a long time thought that the body was homogeneous and consisted of 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane; but the following experiments prove that this is not the case.

Action of Benzoyl Chloride on the Substance, m. p. 173—174°.—One gram of the substance was heated on the water-bath for two hours with excess of benzoyl chloride, the whole shaken with sodium hydroxide solution, extracted with ether, the ethereal solution washed with water until free from alkali, dried over calcium chloride, and the ether evaporated. The solid residue, weighing 1·6 grams, was dissolved in a large amount of absolute alcohol, when, on cooling, 0·4 gram of solid separated (filtrate = *A*) melting at 186—192°, and, after a further crystallisation, at 199°. This substance was proved by the mixed melting point method and by analysis to be identical with the dibenzoyl derivative of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane described on page 77, which latter substance (m. p. 212°) it gave on hydrolysis with alcoholic potassium hydroxide.

The filtrate *A* was evaporated, when several fractions of crystals (in all 1·0 gram) were obtained having the same melting point. These were purified by recrystallisation from ethyl alcohol:

0·1174 gave 0·3335 CO_2 and 0·0892 H_2O. C = 77·48; H = 8·44.

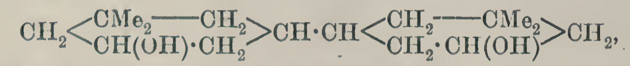
$C_{30}H_{38}O_4$ requires C = 77·92; H = 8·22 per cent.

The *dibenzoyl* derivative of 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane is readily soluble in the cold in benzene or chloroform, moderately soluble in acetone or ethyl acetate, and crystallises from absolute alcohol in radiating clusters of flattened needles melting at 133—134°. When hydrolysed by boiling with alcoholic potassium hydroxide and the solution poured into water, a white solid separated which was purified by recrystallisation from benzene:

0·1071 gave 0·2968 CO_2 and 0·1121 H_2O. C = 75·57; H = 11·63.

$C_{16}H_{30}O_2$ requires C = 77·59; H = 11·81 per cent.

3 : 3′-*Dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldi*cyclo*hexane,*



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CMe_2}\text{——}\mathrm{CH_2}\\ \mathrm{CH(OH)\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CH}<\begin{matrix}\mathrm{CH_2}\text{——}\mathrm{CMe_2}\\ \mathrm{CH_2\cdot CH(OH)}\end{matrix}>\mathrm{CH_2},$$

is readily soluble in the cold in absolute alcohol or acetone, less so in ethyl acetate, crystallises from chloroform or benzene in clusters of scaly needles melting at 183°, and sublimes unchanged in fern-like aggregates of flattened needles. It does not decolorise a chloroform solution of bromine, gives with concentrated sulphuric acid a salmon-pink colour turning to deep orange, and is converted by benzoyl chloride into the above-mentioned dibenzoyl derivative melting at 133—134°, and no other substance.

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* It has since been ascertained that on standing the crystals become opaque and the melting point less sharp. A specimen melting at 173—174°, when first isolated, melted after six weeks at the same temperature, but did not become clear until 180°, and two months later partially melted at 173—174°, but did not clarify until 195°.

On mixing three parts of this product with one part of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane, that is, in the proportion which formed the constant melting mixture (173—174°) of these two substances, the melting point was 172—173°, but complete clarification did not take place until 179°. Moreover, this mixture sublimed in silky needles melting at 171—172° and becoming quite clear at 176°.

Action of Acetyl Chloride on the Substance m. p. 173—174°.—One gram of the substance was heated with an excess of acetyl chloride for two hours, and the solvent evaporated, when the viscous residue so obtained rapidly solidified on rubbing with a few drops of alcohol. It was spread on a porous plate and crystallised from absolute alcohol, when 0·2 gram of needle-shaped crystals separated which melted at 130°, and proved to be identical with the diacetyl derivative of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane described on page 77. On addition of water to the alcoholic mother liquor, further amounts of needle-shaped crystals separated, which were purified by crystallisation from dilute alcohol :

0·1124 gave 0·2916 CO_2 and 0·1060 H_2O. C = 70·75 ; H = 10·47.

$C_{20}H_{34}O_4$ requires C = 71·01 ; H = 10·06 per cent.

The *diacetyl* derivative of 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane is extremely soluble in the ordinary organic media, and crystallises, as above stated, in clusters of slender needles melting at 68°. It is readily hydrolysed by alcoholic potassium hydroxide, yielding 3 : 3′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyldi*cyclo*hexane melting at 183°.

II. *With Sodium in Absolute Alcoholic Solution.*

Twenty grams of chloroketodimethyltetrahydrobenzene were dissolved in 400 c.c. of absolute alcohol in a flask attached to a reverse condenser, and 32 grams of sodium, cut in thin slices, gradually added. At the end of the reaction the whole was poured into a large volume of water, extracted three times with ether, the ethereal solution washed with water, dried over calcium chloride, the ether evaporated, and the residue distilled under diminished pressure, when the following fractions were obtained at 35 mm. :

95—135° = 4·5 grams, 135—150° = 10·7 grams, resinous residue = 1·5 grams.

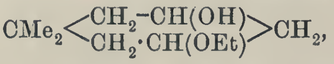
The *fraction* 95—135° gave with sulphuric acid the marked colour reaction characteristic of 3-hydroxy-1 : 1-dimethylhexahydrobenzene (Trans., 1905, **87**, 1495), and no doubt consisted of a mixture of this substance with 3-*hydroxy*-5-*ethoxy*-1 : 1-*dimethylhexahydrobenzene* (see below). The latter compound will, however, form the starting point of another investigation, and a detailed description of its properties and reactions will be reserved for a future communication.

The *fraction* 135—150° was redistilled, when 8 grams of a colourless liquid passed over quite constantly at 135° at 25 mm.:

0·1499 gave 0·3835 CO_2 and 0·1559 H_2O. $C = 69·77$; $H = 11·55$.

$C_{10}H_{20}O_2$ requires $C = 69·76$; $H = 11·62$ per cent.

3-*Hydroxy*-5-*ethoxy*-1 : 1-*dimethylhexahydrobenzene*,



$$CMe_2<\begin{matrix}CH_2\text{-}CH(OH)\\CH_2\cdot CH(OEt)\end{matrix}>CH_2,$$

is a colourless, oily liquid boiling at 135° at 25 mm., and possessing a faint celery-like odour. It does not solidify when cooled in a mixture of ice and hydrochloric acid, does not decolorise a solution of bromine in chloroform, and with concentrated sulphuric acid gives only a very faint orange-pink colour. That it contains an ethoxy-group was proved by a Zeisel determination, carried out according to the directions given by Sir W. H. Perkin (Trans., 1903, **83**, 1367):

0·3445 gave 0·4397 AgI. $-OC_2H_5 = 24·44$.

$C_8H_{15}O\cdot OC_2H_5$ requires $-OC_2H_5 = 26·16$ per cent.

The result is somewhat low, but, as pointed out by Perkin, ethoxy-determinations, as a rule, give results from 1 to 2 per cent. below the calculated.

The *acetyl* derivative, prepared by the action of acetyl chloride, is a colourless, refractive, oily liquid boiling at 129° at 22 mm., and possessing a sweet, slightly camphoraceous odour:

Found, $C = 67·33$; $H = 10·41$.

$C_{12}H_{22}O_3$ requires $C = 67·29$; $H = 10·28$ per cent.

The *benzoyl* derivative, obtained in the usual manner, is a faintly coloured, highly refractive liquid boiling at 226° at 50 mm., and having an odour somewhat resembling that of ethyl benzoate:

Found, $C = 73·75$; $H = 8·85$.

$C_{17}H_{24}O_3$ requires $C = 73·91$; $H = 8·69$ per cent.

III. *With Zinc Dust in Aqueous Alcoholic Solution.*

Two quantities of 29 grams each of chloroketodimethyltetrahydrobenzene were separately dissolved in 108 c.c. of 90 per cent. alcohol, 40 grams of zinc dust mixed with an equal volume of sand added, and the whole heated on the water-bath for four to five hours. The major portion of the alcohol was then distilled off, the residue poured into water, extracted six times with ether, the ethereal solution washed with water, dried over calcium chloride, and the ether evaporated. The residue did not boil constantly (95—102° at 78 mm.), but the major portion passed over between 100—102° at 78 mm., and was analysed with the following result :

0·1403 gave 0·3952 CO_2 and 0·1303 H_2O. C = 76·82 ; H = 10·31.

$C_8H_{12}O$ requires C = 77·42 ; H = 9·67 per cent.

$C_8H_{14}O$,, C = 76·19 ; H = 11·11 ,,

This colourless liquid, which was free from halogen, possessed a pungent, camphoraceous odour, and gave the marked colour reaction with concentrated sulphuric acid characteristic of 3-keto-1 : 1-dimethyl-Δ^4-tetrahydrobenzene (see page 78), but the above analysis proved it to be a mixture of this substance with 3-keto-1 : 1-dimethylhexahydrobenzene * (see page 81), and this is further proved by the fact that on oxidation *as*-dimethylsuccinic acid, the lactone of α-hydroxy-ββ-dimethylglutaric acid, and ββ-dimethyladipic acid were obtained, and by the following experiments.

Nineteen grams of the mixed ketones were dissolved in 52 c.c. of 90 per cent. alcohol, 19 grams of zinc dust and an equal volume of sand added, and the whole heated on the water-bath for ten hours. The major portion of the alcohol was distilled off, the residue poured into water and distilled in steam (residue of distillation = A). The distillate was extracted six times with ether, and the residue obtained on evaporation of the ether again heated with zinc dust in aqueous alcoholic solution ; this process was repeated three times, when it was found that the residue of the steam distillation did not furnish any further solid matter.

The liquid volatile with steam (6 grams) still gave the colour reaction of the unsaturated ketone, and in order to remove these last traces it was treated with dilute potassium permanganate solution in the cold. Only a very small amount of the oxidising agent was used up and the recovered liquid, which boiled quite constantly at 80° at 36 mm., no longer gave a colour with sulphuric acid, and consisted of pure 3-keto-1 : 1-dimethylhexahydrobenzene (see page 81) :

Found, C = 75·87 ; H = 11·14.

$C_8H_{14}O$ requires C = 76·19 ; H = 11·11 per cent.

The semicarbazone crystallised from alcohol in radiating clusters of scaly needles melting at 195° with decomposition and evolution of gas.

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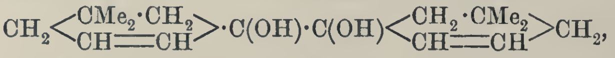
* The action of zinc dust on chloroketodimethyltetrahydrobenzene in the cold gives precisely these same results.

The residue of the steam distillation (*A*) was extracted with ether, the ethereal solution dried over calcium chloride, and the ether evaporated, when 5·7 grams of a viscid, semi-solid mass remained. This and similar material (in all 9·3 grams) from the residues of the other steam distillations were triturated with light petroleum (b. p. 40—60°) and, after filtering, yielded 3·9 grams of a clean, white solid, which after crystallisation from ethyl acetate gave 2·5 grams melting sharply at 148°: *

0·1092 gave 0·3077 CO_2 and 0·1048 H_2O. C = 76·84; H = 10·66.

$C_{16}H_{26}O_2$ requires C = 76·80; H = 10·40 per cent.

1 : 1′-*Dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyl*-$\Delta^{2:2'}$-*di*cyclo*hexene*,



$$CH_2<\begin{matrix}CMe_2\cdot CH_2\\ CH{=\!=}CH\end{matrix}>\cdot C(OH)\cdot C(OH)<\begin{matrix}CH_2\cdot CMe_2\\ CH{=\!=}CH\end{matrix}>CH_2,$$

is fairly readily soluble in the cold in chloroform, benzene, or acetone, less readily in alcohol or ethyl acetate, and crystallises from the latter solvent in stout, transparent, rhombohedral plates melting at 148°. It sublimes unchanged in microscopic, rhombohedral plates, and does not give a colour reaction with sulphuric acid, nor was it found possible to prepare acetyl or benzoyl derivatives under ordinary conditions.

Action of Bromine.—One gram of the substance was dissolved in 15 c.c. of chloroform and a solution of bromine in the same solvent gradually added, when, without the solution becoming appreciably warm, the bromine was rapidly absorbed and torrents of hydrogen bromide evolved. The chloroform was evaporated and the residue (2 grams) purified by crystallisation from benzene:

0·1360 gave 0·2026 CO_2 and 0·0560 H_2O. C = 40·63; H = 4·57.

0·1102 „ 0·1316 AgBr. Br = 50·81.

$C_{16}H_{21}OBr_3$ requires C = 40·93; H = 4·47; Br = 51·17 per cent.

The *tribromoanhydride* (?) of dihydroxytetramethyldi*cyclo*hexene is very slightly soluble, even on boiling in alcohol, acetone, or ethyl acetate, but is sufficiently soluble to be crystallised from either benzene or chloroform, when it separates in small, glistening, flattened needles, which on heating in a capillary tube begin to darken at 245° and melt with complete decomposition at 250°. It only dissolves slowly when heated with fuming nitric acid, and, on cooling, faintly yellow, scaly needles separate, melting at 212° with decomposition, but no more definite information can be given at the present time owing to lack of material.

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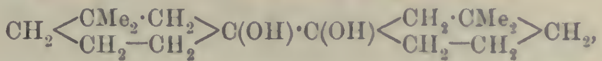
* There is a second product of lower melting point present in this and also in the solid isolated from the action of zinc dust and acetic acid on chloroketodimethyltetrahydrobenzene (see p. 83), but up to the present time it has not been found possible to draw any very definite conclusions as to the constitution of this substance, though it certainly possesses the formula $C_{16}H_{26}O_2$.

Action of Sodium in moist Ethereal Solution.—Two grams of dihydroxytetramethyldi*cyclo*hexene were dissolved in a mixture of 20 c.c. of alcohol and 40 c.c. of ether, the solution floated on 30 c.c. of water, and 12 grams of sodium, cut in very thin slices, gradually added. As the reaction proceeded, a white solid separated which dissolved on the addition of further small amounts of alcohol and ether. The major portion of the solvents was then evaporated, the residue poured into water, the solid which separated, filtered, washed with water, spread on plate (2·3 grams), and crystallised from ethyl acetate :

0·1077 gave 0·2985 CO_2 and 0·1154 H_2O. $C = 75·58$; $H = 11·90$.

$C_{16}H_{30}O_2$ requires $C = 75·59$; $H = 11·81$ per cent.

1 : 1′-*Dihydroxy*-5 : 5 : 5′ : 5′-*tetramethyldi*cyclo*hexane*,



$$CH_2{<}\begin{matrix}CMe_2\cdot CH_2\\CH_2-CH_2\end{matrix}{>}C(OH)\cdot C(OH){<}\begin{matrix}CH_2\cdot CMe_2\\CH_2-CH_2\end{matrix}{>}CH_2,$$

is but slightly soluble in chloroform or benzene, not readily so in acetone, alcohol, or ethyl acetate, and crystallises from the latter solvent in transparent, oblique, square plates melting at 212°. It sublimes unchanged in fern-like aggregates, and does not give a colour reaction with concentrated sulphuric acid. Although so readily formed by the action of sodium in moist ethereal solution on dihydroxytetramethyldi*cyclo*hexene, no trace of it could be found on heating the latter substance for twelve hours with zinc dust in aqueous alcoholic solution.

The *diacetyl* derivative, prepared by the direct action of acetyl chloride, is readily soluble in the cold in benzene, chloroform, acetone or ethyl acetate, and crystallises from alcohol in sheaves of needles or on slow crystallisation in well-formed rectangular prisms melting at 130° :

Found, $C = 70·99$; $H = 10·31$.

$C_{20}H_{34}O_4$ requires $C = 71·00$; $H = 10·06$ per cent.

The *dibenzoyl* derivative, prepared as described on page 72, is readily soluble in the cold in benzene or chloroform, moderately soluble on heating in alcohol or acetone, and crystallises from ethyl acetate in transparent, four-sided plates melting at 199° :

Found, $C = 77·82$; $H = 8·26$.

$C_{30}H_{38}O_4$ requires $C = 77·92$; $H = 8·22$ per cent.

Both the diacetyl and dibenzoyl derivatives regenerate dihydroxytetramethyldi*cyclo*hexane (m. p. 212°) when hydrolysed with alcoholic potassium hydroxide.

IV. *With Zinc Filings in Aqueous Alcoholic Solution.*

Twenty grams of chloroketodimethyltetrahydrobenzene were dissolved in 108 c.c. of 90 per cent. alcohol, 30 grams of zinc filings added, and the whole heated on the water-bath, during which time zinc chloride separated. The heating was continued for five hours, when the major portion of the alcohol was distilled off, the residue poured into water, the solution extracted six times with ether, the ethereal solution washed once with water, dried over calcium chloride, and the ether evaporated. The residue was again treated with zinc filings and 90 per cent. alcohol, and the whole process repeated six times, when the resulting liquid was found to be practically free from halogen. On distilling under diminished pressure, the major portion (free from halogen) passed over quite constantly at 89·5° at 30 mm., leaving a small residue which contained chlorine. This fraction was again distilled and analysed:

0·1227 gave 0·3471 CO_2 and 0·1078 H_2O. C = 77·15; H = 9·76.

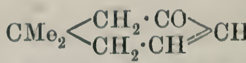
$C_8H_{12}O$ requires C = 77·42; H = 9·67 per cent.

As the yield of the ketone prepared in this manner is not very satisfactory, the reaction was tried in the cold, when the amount formed is considerably increased, as is also the case when using the zinc-copper couple. For this purpose 10 grams of chloroketodimethyltetrahydrobenzene were dissolved in 15 c.c. of 90 per cent. alcohol, 10 grams of zinc-copper couple added, and the whole allowed to stand at the ordinary temperature, when zinc chloride rapidly separated. After forty-eight hours it was filtered (filtrate = *A*), the residue washed with alcohol, the alcoholic solution evaporated, added to *A*, which was again treated with the zinc-copper couple and this process repeated four times, when the addition of fresh zinc-copper couple did not produce any further separation of zinc chloride. The whole was then poured into water and worked up as described above. On distilling the residue under diminished pressure, it passed over for the most part quite constantly, leaving but a small residue which contained chlorine, and after a second distillation it boiled at 83·5° at 25 mm.:

0·1183 gave 0·3349 CO_2 and 0·1066 H_2O. C = 77·21; H = 10·01.

$C_8H_{12}O$ requires C = 77·42; H = 9·67 per cent.

As large quantities of this ketone are being prepared for another investigation, a description of the best method of obtaining it is reserved for a future communication.

3-*Keto*-1 : 1-*dimethyl*-Δ^4-*tetrahydrobenzene*,  $CMe_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH\end{matrix}>CH$, is a colourless, highly refractive liquid, boiling at 88·5° at 32 mm., and possessing an odour of almonds, which soon becomes disguised by a pungent smell of camphor. When treated with an equal bulk of concentrated sulphuric acid it gives a blood-red colour, turning to plum-red, then gradually to violet and finally disappears. A solution of bromine in chloroform is immediately decolorised on addition of a chloroform solution of the ketone, and an attempt was made to determine the bromine absorption value, but without success, for although there is an apparent end reaction when 1 molecule of bromine has been added, yet at this point hydrogen bromide is evolved, and the amount increases rapidly with further addition of bromine.

The *semicarbazone* prepared by adding the ketone to a concentrated alcoholic solution of semicarbazide acetate, crystallises from methyl alcohol in nacreous scales melting at 195° to a clear yellow liquid which slowly evolves gas. The preparation requires to be carried through as rapidly as possible on account of the ease with which the semicarbazone decomposes, especially when in solution :

Found, N = 23·39. $C_9H_{15}ON_3$ requires N = 23·20 per cent.

Action of Hydroxylamine.—Two grams of hydroxylamine hydrochloride were dissolved in the smallest amount of water, alcohol and 2 grams of the ketone added, the solution neutralised with sodium hydroxide and allowed to stand twelve hours. It was then poured into a saturated solution of brine, the whole extracted with ether, the ethereal solution washed with water, carefully dried over calcium chloride, and the ether distilled off. As the slightly coloured residue showed no sign of solidification on standing or on cooling, and as, unlike the oxime of the corresponding saturated ketone (see page 81), it could not be distilled even under a low pressure without complete decomposition, the nitrogen was determined in a specimen of the liquid prepared as above described :

Found, N = 11·15. $C_8H_{13}ON$ requires N = 10·07 per cent.

Although the nitrogen found is not very closely in accord with the calculated amount, it is sufficiently near to show that the substance is a simple oxime and not a hydroxylamino-oxime, which would require 16·27 per cent. of nitrogen.

Moreover, when the crude oxime was treated with benzoyl chloride, although decomposition took place resulting mainly in the formation of a dark coloured liquid, a small quantity of a solid benzoyl derivative was isolated, crystallising from absolute alcohol in nacreous, scaly needles melting at 171—172° and containing 6·10 per cent. of nitrogen, whereas the calculated amount for the benzoyl derivative of the simple oxime is 5·76 per cent.

Oxidation of the Ketone.—Five grams of the ketone were suspended in 125 c.c. of water, and a cold saturated solution of potassium permanganate added until no longer decolorised. As oxidation took place very rapidly, the solution was cooled by the addition of small quantities of ice and then worked up in the usual way, when 5·2 grams of a white solid were obtained. This was dissolved in water and the solution saturated with hydrogen chloride, when, on standing, 1·8 grams of needle-shaped crystals separated melting at 139—140°, nor was this melting point lowered on mixing with pure *as*-dimethylsuccinic acid. The identity of this substance was further proved by converting a portion into the anilic acid, which crystallised from methyl alcohol in nacreous, scaly needles melting at 187° with evolution of gas.

The mother liquor from the *as*-dimethylsuccinic acid was evaporated to dryness, and the solid residue (2·5 grams) heated with excess of acetyl chloride for two hours. On evaporation of the solvent, the residue solidified rapidly when stirred, and after frequent crystallisation from benzene was obtained in stellar aggregates of transparent needles melting at 110—111°:

0·1100 gave 0·2142 CO_2 and 0·0654 H_2O. C = 53·10; H = 6·60.

$C_7H_{10}O_4$ requires C = 53·16; H = 6·33 per cent.

0·2019 required 12·85 c.c. *N*/10 NaOH. Calculated, 12·78 c.c.

$C_7H_{10}O_4$ molecular weight calculated 158. Found, 157.

On heating the solution used for this titration, a further 11·5 c.c. of *N*/10 NaOH were required for neutralisation. This substance is evidently, therefore, the lactone of α-hydroxy-ββ-dimethylglutaric acid (compare Perkin and Thorpe, Trans., 1899, **75**, 56).

V. *With Zinc Dust in Acetic Acid Solution.*

Two quantities of 20 grams of chloroketodimethyltetrahydrobenzene were separately dissolved in 80 grams of glacial acetic acid contained in a flask attached to a reverse condenser and heated on a sand-bath. Thirty-three grams of zinc dust were gradually added, at first in very small amounts as the reaction is a vigorous one. The operation takes about twenty hours, at the end of which time the whole was neutralised with sodium hydroxide and distilled in steam (residue = *A*), the distillate extracted six times with ether, the ethereal solution washed with potassium hydroxide, then with water, dried over calcium chloride, and the halogen free residue obtained on evaporation of the ether distilled under low pressure and analysed:

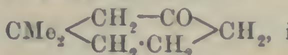
0·1080 gave 0·3017 CO_2 and 0·1090 H_2O. C = 76·18; H = 11·21.

$C_8H_{14}O$ requires C = 76·19; H = 11·11 per cent.

The same substance may be obtained by using dilute instead of glacial acetic acid. For this purpose, 20 grams of chloroketodimethyltetrahydrobenzene were dissolved in 48 grams of glacial acetic acid and 40 c.c. of water and treated with 33 grams of zinc dust. Towards the end of the reaction it was necessary to add small quantities of glacial acetic acid. The product was worked up as described above, when the steam distillate (residue of distillation = *B*) yielded a liquid boiling at 77·5° at 27 mm:

0·1316 gave 0·3660 CO_2 and 0·1319 H_2O. C = 75·85; H = 11·13.
$C_8H_{14}O$ requires C = 76·19; H = 11·11 per cent.

The only difference between this specimen of the ketone and that prepared by the action of glacial acetic acid was that the former gave a faint colour reaction indicative of the presence of the corresponding unsaturated ketone (see page 75). The amount present must have been extremely small, as it did not affect the above quoted analysis, and after treating this specimen of the ketone in the cold with dilute potassium permanganate it no longer gave the colour reaction.

3-*Keto*-1 : 1-*dimetylhexahydrobenzene*,  $CMe_2<\begin{matrix}CH_2—CO\\CH_2·CH_2\end{matrix}>CH_2$, is a clear, colourless, refractive liquid boiling at 75·5° at 25 mm. and possessing a strong camphoraceous odour. The yield when using glacial acetic acid is 50—55 per cent. of the theoretical amount, and with dilute acetic acid somewhat less. The ketone does not give a colour reaction with sulphuric acid. When dissolved in chloroform and a solution of bromine in the same solvent added, no bromine is absorbed for some little time, then the colour suddenly disappears, hydrogen bromide is evolved, and on adding more bromine it is rapidly absorbed and torrents of hydrogen bromide are given off. This seems, perhaps, an unusual behaviour for a saturated compound, but it has been ascertained that ketohexahydrobenzene behaves in exactly the same way towards bromine, and the phenomenon is probably connected with the conversion of the bodies into derivatives of the aromatic series, a point which is receiving attention.

The *semicarbazone*, prepared in the usual manner, crystallises from absolute alcohol in radiating clusters of glistening, flattened needles melting at 195° with evolution of gas and much greater decomposition than the semicarbazone of the corresponding unsaturated ketone (see page 79):

Found, N = 22·72. $C_9H_{17}ON_3$ requires N = 22·95 per cent.

The *oxime* was prepared from 5 grams of the ketone exactly as described on page 79. It distilled quite constantly at 132° at 37 mm. as a clear, colourless, syrupy liquid with a sickly odour somewhat reminiscent of both camphor and celery:

Found, N = 9·83. $C_8H_{15}ON$ requires N = 9·93 per cent.

As it did not solidify on cooling or on standing for some considerable time, it was converted into the *benzoyl* derivative, which is readily soluble in the cold in the usual organic solvents, but crystallises from dilute alcohol in nacreous scales melting at 69° :

Found, N = 6·05. $C_{15}H_{19}O_2N$ requires N = 5·71 per cent.

This substance was then hydrolysed by warming with potassium hydroxide (1 : 2), when suddenly the solution became quite clear, and on passing carbon dioxide through it the oxime was precipitated. It was extracted with ether, &c., when, on standing some time in a vacuum, it solidified completely. The solid melted at 43—44°, was extremely soluble in the cold in the usual organic media, and was proved by analysis to consist of the pure oxime.

Oxidation of the Ketone.—Ten grams of the ketone were suspended in 250 c.c. of water and a saturated solution of potassium permanganate gradually added. The oxidising agent was only used up extremely slowly in the cold, and therefore the whole was heated on the water-bath, when the reaction required about forty hours for completion. The product was treated in the usual way, yielding 5 grams of solid, which were dissolved in water and the solution saturated with hydrogen chloride, but even on long standing no crystals were deposited (compare Trans., 1906, **89**, 1552). The solution was evaporated, care being taken to get rid of all the hydrogen chloride, and the residue crystallised from a mixture of chloroform and light petroleum, when 2·8 grams of radiating clusters of rhombic plates separated, melting at 85—86°, nor was this melting point lowered on mixing with pure ββ-dimethyladipic acid :

0·1193 gave 0·2411 CO_2 and 0·0879 H_2O. C = 55·12 ; H = 8·18.

$C_8H_{14}O_4$ requires C = 55·17 ; H = 8·04 per cent.

On evaporating the mother liquor from the dimethyladipic acid, there remained a solid residue, which was dissolved in water and the solution saturated with hydrogen chloride, but on standing only a few minute crystals separated. These were filtered and hydrogen chloride allowed to escape from the solution, when compact crystals formed, consisting of pure ββ-dimethyladipic acid, thus proving that only minute traces of the isomeric αα-dimethyladipic acid could have been produced during the oxidation.

The residue from the steam distillation *A* (see page 80) was acidified with acetic acid, extracted with ether, the ethereal solution washed with potassium hydroxide solution, then with water, dried over calcium chloride, and the ether evaporated, when a residue of 9·2 grams remained which partially solidified. This was triturated with light petroleum (40—60°), yielding 3 grams of solid, from which on crystallisation from ethyl acetate there were obtained 2 grams of pure 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyl-$\Delta^{2:2'}$-di*cyclo*hexene (see page 76). The residue from the steam distillation *B* (see page 80) was treated in a similar manner, except that the trituration with light petroleum was unnecessary, when it yielded 1·4 grams of 1 : 1′-dihydroxy-5 : 5 : 5′ : 5′-tetramethyl-$\Delta^{2:2'}$-di*cyclo*hexene.

Both the above solid residues from *A* and *B* contained a large proportion of the low melting solid referred to in the footnote on page 76.

The authors take this opportunity of expressing their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

RESEARCH LABORATORY, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.

VII.—*The Viscosity of Liquid Mixtures.*

By ALBERT ERNEST DUNSTAN and ROBERT WILLIAM WILSON.

IN the two previous parts of this series, the viscosity concentration curves of various liquid mixtures have been investigated, and it has been shown that these curves could be divided into three classes :

(i) Those approximately obeying the law of mixtures, being concave to the axis of percentage composition, and having the greatest divergence from normal at some point of simple molecular concentration.

(ii) Those exhibiting definite maxima at points corresponding with mixtures of simple molecular composition. Nearly all experimental work in this class has been done with aqueous solutions, and a great volume of evidence points to the conclusion that in such mixtures the formation of hydrates is always existent, producing groups of complexes in dynamic equilibrium even when definite compounds cannot actually be isolated.

(iii) Those exhibiting minima which also are to be found at points of simple molecular composition.

In general, these liquid pairs which are made up of unimolecular non-associating components give viscosity concentration curves which, although frequently near the normal, yet sometimes diverge considerably from it.

In the present communication, a brief account is given of certain empirical relationships which hold good for these viscosity concentration curves (*Zeit. physikal. Chem.*, 1906, **56**, 370), and further experimental results in the shape of a curve for mixtures of water and sulphuric acid are adduced.

It has been laid down in previous papers that increase in the viscosity coefficients implied increase in the masses of the colliding slipping particles whether they be simple molecules or loosely held complexes. Whereas, on the one hand, carbon disulphide, ether, the paraffins and other simple unimolecular liquids are mobile, the alcohols and acids are more viscous, glycol and glycerol notably so, whilst the comparatively enormous molecular masses of the jellies and colloids attain an almost infinite viscosity.

A decrease in viscosity similarly may imply a decrease in complexity or the disintegration of the molecular groupings in solution, and this phenomenon is sometimes observed even when a more viscous compound is added to one of less viscosity.

The experimental data in this work have been obtained in the same manner as in previous papers. The sulphuric acid was kindly supplied in considerable quantity by Dr. Messel, to whom we are glad of this opportunity of expressing our gratitude.

The two specimens of this acid which we obtained were of special purity. The strength was determined by titration of the diluted acid, by conversion into barium sulphate, and from the density, using Pickering's tables (Trans., 1890, **57**, 64).

Analysis of the first specimen:

By density .... $H_2SO_4 = 99{\cdot}5$ per cent.
By titration......... $H_2SO_4 = 99{\cdot}2$,,
Gravimetrically ... $H_2SO_4 = 99{\cdot}57$,,

The second specimen gave as average of density determinations:

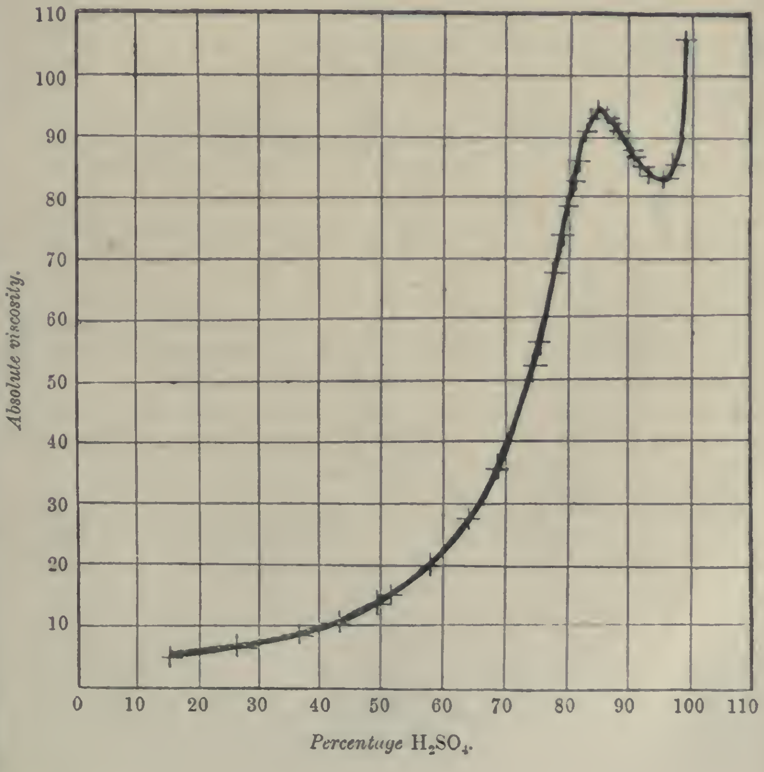
$$H_2SO_4 = 99{\cdot}924 \text{ per cent.}$$

The water used was redistilled from alkaline permanganate and kept in well-stoppered Jena flasks. A large stock of 50 per cent. acid was made, and this served for the middle determinations by addition either of water or acid. The strengths of the solutions were determined mainly by Pickering's tables of density; frequent checks were made by titration and also by gravimetric analysis.

The following table gives the percentage composition of the solutions, the density and the viscosity coefficients. These data are plotted on the accompanying curve (Fig. 1):

H_2SO_4 per cent.	Density.	Viscosity.
99·924	1·82714	1·06160
97·513	1·83171	0·85761
95·723	1·82986	0·83255
93·410	1·82348	0·84211
92·300	1·81930	0·85088
91·363	1·81476	0·87158
90·437	1·80982	0·88508
89·575	1·80525	0·95132
88·733	1·79985	0·91588
88·001	1·79522	0·92568
86·865	1·78650	0·93366
86·979	1·78737	0·93527
85·070	1·77160	0·94794
84·970	1·77074	0·92966
84·280	1·76447	0·92529
83·980	1·76069	0·91010
83·401	1·75588	0·90866
82·580	1·74750	0·89842
82·210	1·74384	0·86571
81·544	1·73719	0·83108
81·086	1·73197	0·83452
80·243	1·72287	0·78099
79·838	1·71844	0·60272
79·528	1·71484	0·74084
78·242	1·70030	0·67228
76·271	1·67756	0·57396
74·746	1·65976	0·53603
70·519	1·61049	0·40095
69·205	1·59488	0·36450
67 209	1·57236	0 32322
64·643	1·54331	0·28042
58·356	1·47457	0·20568
51·640	1·40596	0·15370
49·858	1·38857	0·14706
43·234	1·32691	0·11293
36·427	1·26759	0·09239
26·492	1·18630	0·07119
15·699	1·10413	0·05851
0	0·99717	0·00891

FIG. 1.



In a useful summary of work done on the question of the molecular constitution of solutions of sulphuric acid, Burt (Trans., 1904, **85**, 1351) points out that the conclusion that combination takes place in such solutions with the formation of complexes had been arrived at mainly by cryoscopic methods.

Pickering (Trans., 1890, **57**, 64, 331), in his classical investigation on this subject, brings forward indisputable evidence as to the existence of such complexes, an existence which in the case of some he proves by their actual isolation. With respect to density determinations, Pickering quotes Mendeléeff's experimental curves (*Zeit. physikal. Chem.*, 1887, **1**, 275; see also Crompton, Trans., 1888, **53**, 116) in which after differentiation the following hydrates were deduced: H_2SO_4,H_2O, $H_2SO_4,2H_2O$, $H_2SO_4,6H_2O$, $H_2SO_4,150H_2O$.

Pickering's own curve after a similar process afforded seventeen straight lines equivalent to a complex first curve of seventeen parabolic components, which the author considered as the density curve of seventeen hydrates in solution. From the contractions on mixing, similar discontinuous sections identical with the above were found.

He investigated Kohlrausch's conductivity curves, which gave five hydrates, and obtained the same results.

Jones (*J. Amer. Chem. Soc.*, 1894, **16**, 1), by investigating the lowering of the freezing point of acetic acid by sulphuric acid, claimed to have proved the existence of H_2SO_4,H_2O and $H_2SO_4,2H_2O$ in solution. That the former hydrate is capable of existence and isolation is no longer doubted.

Pictet (*Compt. rend.*, 1894, **119**, 642) obtained, by the cryoscopic method, maximum and minimum points corresponding with H_2SO_4,H_2O, $H_2SO_4,2H_2O$, and others.

Ramsay and Shields (Trans., 1894, **65**, 179) found that the constant boiling liquid $12H_2SO_4,H_2O$ had an abnormally high molecular weight and concluded that complexes had been formed.

Graham's work (*Phil. Trans.*, 1846, *A*, 513; 1861, 373) on solutions of sulphuric acid and water brought out quite clearly the maximum at 85·1 per cent. of the acid corresponding with H_2SO_4,H_2O; the remainder of the curve on both sides of this point is quite normal.

Burt's own conclusions (*loc. cit.*) drawn from his results on the vapour pressures of sulphuric acid solutions are of great interest; he points out that:

(1) The molecular weights calculated from the vapour pressures never rise above 32·7.

(2) The molecular weights usually lie below 32·7, increase with temperature, and decrease with greater concentration.

(3) Inversion points are of frequent occurrence in the curves of

molecular weight × temperature. He concludes that complexes are formed, but finds no evidence for the existence of definite hydrates.

Knietsch (*Ber.*, 1901, **34**, 4069) made an elaborate investigation of these mixtures, using not only determinations of viscosity, but also of the melting points, conductivities, and surface tensions.

From the melting-point curve, he deduced the existence of H_2SO_4,H_2O, and H_2SO_4,SO_3 at maxima, and of $2H_2SO_4,H_2O$, $4H_2SO_4,SO_3$, and $H_2SO_4,2SO_3$ at minima.

From the conductivity numbers, he found discontinuities at points corresponding with H_2SO_4,H_2O, and $2H_2SO_4,H_2O$, and at 15 per cent. free SO_3.

The viscosity data show that the effect of adding sulphuric acid to water in gradually increasing amount is to cause an equally gradual increase in the viscosity. The first maximum point is attained at 85 per cent., that is, the "monohydrate," but it is to be noticed that the increase in the viscosity is by no means commensurate with the simple addition of H_2O to H_2SO_4 or of H_2SO_4 to H_2O.

So far as can be seen from the previous work on aqueous solutions, these maxima would more probably correspond to aggregates such as $(H_2SO_4,H_2O)_n$, where "n" may be of considerable magnitude.

As will be noticed in the sequel, a very rough approximation for the addition of CH_2 in an homologous series is 0·001 unit of viscosity. Thus toluene to xylene, methyl to ethyl iodide, hexane to heptane, ethyl bromide to propyl bromide give such increments. Larger increments are found in the alcohol and acid series, but in the case we are considering, the minimum point viscosity is 0·083255, and the maximum point 10 per cent. from it is 0·094794, whilst water is 0·00891. From this maximum, further addition of water reduces the viscosity to a minimum which is located at about 95 per cent.; after this point the viscosity again steadily increases through H_2SO_4 until the second maximum at 50 per cent. free SO_3 (Knietsch, *loc. cit.*), both maxima corresponding with the two maxima of density.

It will be noticed that in the appended curve there is a minimum point at 95 per cent. corresponding with $3H_2SO_4,H_2O$.

A similar minimum point was obtained with mixtures of benzaldehyde and alcohol and with benzene and alcohol. Such a point can be interpreted as being the final result of the fission of sulphuric acid complexes by the water, the fission being complete when the water reaches the above concentration. The addition of more water causes more complex formation until this culminates in the building up of the monohydrate, which, at any rate in solution, may be the first anhydride of orthosulphuric acid. The position of this well-known compound is clearly indicated at 85 per cent. No further well-marked discontinuity occurs, at any rate, of the same order as the maximum already quoted.

Possibly more delicate apparatus would indicate such complexes of the "second order." The position of sulphuric acid and its "monohydrate" on the viscosity-molecular weight curves (v.s.) indicates the high degree of association it possesses.

It will be readily seen from what has gone before that little obedience to the mixture law can be expected from two components like sulphuric acid and water, alcohol and benzene, or, in brief, wherever we deal with associated substances, and it is because of this reciprocal action of one on the other that all attempts to investigate these effects have failed. The formula given by Lees (*Phil. Mag.*, 1901, [vi], 1, 128), $\eta^n = v_1\eta_1{}^n + v_2\eta_2{}^n$, where "$n$" is a constant for the liquid pair, η, η_1, and η_2 the viscosity coefficients for the mixture, and the two components respectively, and $v_1 v_2$ the relative volume of the two components, fits in most closely with observed facts; at the same time it should be noticed that this can scarcely be described as a mixture law which has to be qualified in each case.

Several regularities have been met with in the course of this investigation, especially in connexion with unimolecular liquids.

A. *Connexion between Molecular Weight and Angle between Tangent to Curve and Axis of Viscosity.*

In any of the previously given curves (Trans., 1904, **85**, 817; 1905, **87**, 11) let tangents be drawn at the point where the curve meets the viscosity axis.

Let α be the angle between the tangent and the viscosity axis.

Then α is connected with the molecular weight of the liquid in question, as follows:

TABLE I.

Solution in benzene.	Mol. wt.	α.	Product.	Solution in alcohol.	Mol. wt.	α.	Product.
Carbon tetrachloride	154	52	7·9	Carbon disulphide	76	128	9·73
Toluene	92	93	8·55	Mercaptan	62	148	9·17
Ethyl acetate	88	94	8·27	Acetone	58	100	5·8
Carbon disulphide	76	105	7·98	Benzene	78	48	3·72
Ethyl ether	74	102	7·55	Benzaldehyde	106	62	6·57

It is to be noticed that the last three alcoholic solutions give abnormal experimental results, in that minima or exceptionally sagged curves are shown.

If such behaviour indicates dissociation, then the associated benzaldehyde and benzene having a greater molecular mass than normal would, as shown in the sequel, give a steeper curve and a smaller angle α. In all cases examined, the viscosity concentration curves are parabolic, and can be fairly represented by

$$x = ay^2 + by + c,$$

$$\text{therefore } \frac{dx}{dy} = Ky + M,$$

hence a relation exists between the tangent of a and y, that is, the viscosity coefficient, or, as is shown here, between a and molecular weight.

B. *Connexion between Molecular Weight and Viscosity.*

The following table (Dunstan, *Zeit. physikal. Chem.*, 1905, **51**, 738) further shows the close connexion between molecular weight and viscosity, and also illustrates the great abnormality of the hydroxylated liquids (see Thorpe and Rodger, *Phil. Trans.*, 1897, **185**, *A*, 397):

Liquid.	η/M.V. × 10^6.	Liquid.	η/M.V. × 10^6.
Benzene	65	Water	493
Ethyl acetate	60	Methyl alcohol	138
Ethyl iodide ...... -	69	Ethyl ,, ...	189
Ethyl bromide	51	Propyl ,, ...	262
Chloroform	67	Allyl ,, ...	180
Acetone	43	Glycol	2750
		Benzaldehyde	143
		Acetic acid	195
		Lactic ,, ...	5410

A further relationship may be deduced from the viscosity concentration curves given in previous communications (*loc. cit.*).

Taking again tangents to these curves at the vertical axes and calling the angles between the curve and tangent "*b*" and "*c*" respectively, then the following statement holds good. The product of the molecular weight of each liquid with the angle "*c*" or "*b*" is constant, for the effect of liquid *A* on liquid *B* is measured by the angle "*b*" and *vice versâ*, the effect of *B* on *A* is measured by the angle "*c*":

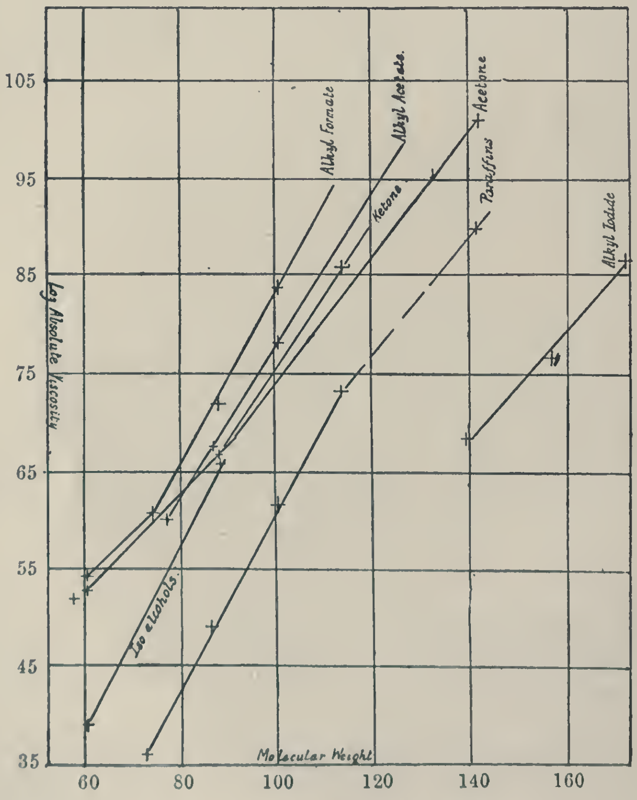
TABLE II.

Liquid *A*.		$\angle b$.	Liquid *B*.		$\angle c$.	$\frac{A\angle c}{B\angle b} = K$.
Ethyl mercaptan	62	16	Ethyl alcohol	46	13	$\frac{806}{736} = 1{\cdot}09$
Toluene	92	2	Benzene	78	2	$\frac{184}{156} = 1{\cdot}18$
Carbon disulphide......	76	2	Methyl iodide	142	4	$\frac{304}{284} = 1{\cdot}07$
Ethyl ether	74	12	Benzene	78	15	$\frac{1110}{936} = 1{\cdot}18$
Carbon disulphide......	76	3	Benzene	78	3	$\frac{228}{234} = 0{\cdot}97$
Ethyl acetate............	88	13	Benzene	78	12	$\frac{1056}{1014} = 1{\cdot}04$

C. *Relation between Molecular Weight and Viscosity of Series of Compounds.*

An important connexion between these quantities is evidenced when they are plotted as in Fig. 2, log. viscosity against molecular weight. It will be seen that the various members of a chemical series lie on the same curve. The viscosity-molecular weight curves are parabolic. The simple esters lie closely together, and there is a similar proximity between the symmetrical and asymmetrical ketones. Chloroform is placed near the paraffins. The paraffins investigated by Thorpe and Rodger lie almost on a straight line; other available determinations show a considerable want of agreement with these and with themselves.

Fig. 2.

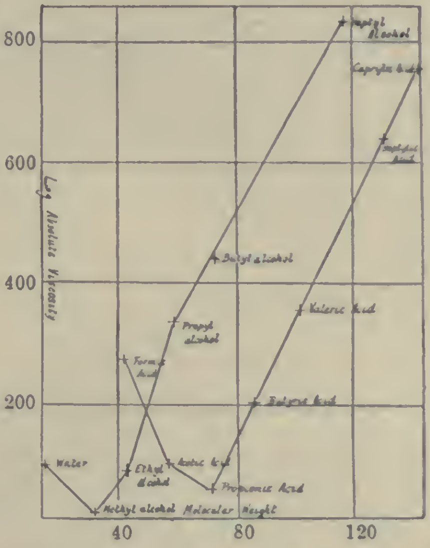


It is to be noticed that the first members of each series diverge more or less from the logarithmic line and behave as though they had a larger molecular weight than normal (see also, for this association of the early members of homologous series, Ramsay and Shields, Trans., 1893, **53**, 1101).

Benzene also occupies an anomalous position, giving evidence of considerable association (nearly 110 mol. wt.).

Fig. 3 shows the logarithmic curves for the acids and alcohols. The two curves are very similar and indicate the same inconsistent behaviour of the earliest members; from the points given by water and formic acid the curves follow almost parallel to each other. A consideration of these curves will show that water behaves as a liquid of molecular weight nearly 50, that is, $(H_2O)_3$, and formic acid nearly 100, that is, $(H{\cdot}CO_2H)_2$, assuming that the other members are normal. Hence we may deduce the general law:

FIG. 3.



$$\gamma = A + B \log. \eta,$$

where γ is the molecular weight, A and B are constants depending on the particular series to which the liquid belongs, and η is the viscosity coefficient.

It will be noticed that B, which measures the slope of the curves, is almost the same in the various series, and has therefore a general nature, A being the specific constant for each family.

The authors desire to thank Prof. Trouton for his interest in this investigation.

EAST HAM TECHNICAL COLLEGE. UNIVERSITY COLLEGE.

VIII.—*Relation between Chemical Constitution and Physiological Action in the Tropeines.*

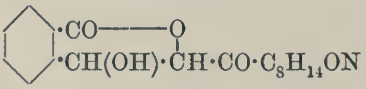
By Hooper Albert Dickinson Jowett and Frank Lee Pyman.

In a previous communication (Trans., 1906, **89**, 357) it was shown by one of us, in conjunction with Mr. Hann, as the result of the physiological examination of a number of new tropeines:

(1) That the peculiar difference in physiological action between a lactone and its corresponding hydroxy-acid, as exemplified by pilocarpine and pilocarpic acid, also occurs in the case of a tropeine having a haptophore group similar to that in pilocarpine, namely, terebyltropeine, and also in the case of phthalidecarboxyltropeine.

(2) That Ladenburg's generalisation, so far as it refers to the necessity for a mydriatic tropeine to contain a benzene nucleus, does not strictly hold since terebyltropeine possesses a distinct mydriatic action.

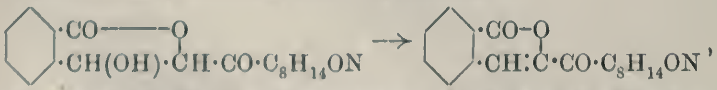
In order further to elucidate these two points the following tropeine was prepared and physiologically examined:



Lactone of o-*Carboxyphenylglyceryltropeine.*

If Ladenburg's generalisation is valid, namely, that a tropeine to possess mydriatic properties must contain an acyl group attached to a benzene nucleus, and an aliphatic hydroxyl in the side-chain containing the carboxyl group, and if the observation that a lactone is much more active physiologically than the corresponding hydroxy-acid applies also in this instance, then the above tropeine should be a very powerful mydriatic, for it fulfils the requirements of Ladenburg's generalisation and is also a lactone. Its corresponding hydroxy-acid would contain two hydroxyl groups in the side-chain bearing the carboxyl, and the lactone of such a compound might naturally be expected to prove very active physiologically.

It was found that this tropeine, on heating, readily lost the elements of water, forming iso*coumarincarboxyltropeine*,



in a manner similar to the conversion of the lactone of *o*-carboxyphenylglyceric acid into *iso*coumarincarboxylic acid (Bamberger and Kitschelt, *Ber.*, 1892, **25**, 896).

This lactone was examined physiologically, and it was also thought to be of interest to prepare and examine physiologically certain alkyl bromides of these tropeines, as well as those of homatropine.

The necessary physiological experiments were conducted in the Wellcome Physiological Research Laboratories by Mr. C. T. Symons, to whom we wish to tender our best thanks, and he reports as follows:

The tropeines were slightly mydriatic. No effect was observed on instillation of aqueous solutions into the conjunctival sac, but a certain degree of mydriasis was produced by intramuscular injection; in this respect, therefore, they were very much weaker than homatropine or atropine. Experiments were also made to determine their action on the vagus nerve-endings in the heart, and in this respect also they proved to be much less active than atropine.

With regard to their action as lactones it was found that, similarly to pilocarpine (compare Marshall, *J. Physiol.*, 1904, **31**, 153), they lost their action on the vagus nerve-endings in the heart after a molecular proportion of alkali had been added to the base, this change of activity being undoubtedly due to the conversion of the lactone into its corresponding hydroxy-acid.

With regard to the alkyl derivatives of these tropeines, it was found that distinct differences in activity exist between the hydrobromides on the one hand and their corresponding methobromides on the other. As has been observed before with other alkaloids, so here, the introduction of a methyl group, forming a quaternary nitrogen base, very much diminishes the action of the substance on nerve centres, and induces a more curare-like action on the motor nerve-endings in voluntary muscle. This is particularly noticeable in a comparison between the hydrobromide and the methobromide of the lactone of *o*-carboxyphenylglyceryltropeine, and also appears in a less pronounced degree in the case of *iso*coumarincarboxyltropeine.

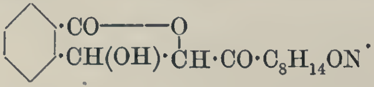
The alkyl salts of homatropine were compared with homatropine hydrobromide as regards the mydriatic action produced on instillation of 0·5 per cent. solutions into the conjunctival sac, and it was found that the pupils of cats' eyes were dilated more completely and more quickly by the methobromide and methonitrate than by the hydrobromide, but only very slightly by the ethobromide.

The results of this investigation confirm and amplify the conclusions previously arrived at (*loc. cit.*), and prove that Ladenburg's generalisation cannot be maintained, since it does not hold good in the case of terebyltropeine, which is mydriatic although not conforming to the generalisation, nor in the case of the lactone of *o*-carboxyphenylglyceryltropeine, which should according to the theory be very active, but does not prove to be so.

On the other hand, the difference in activity between the lactone and its corresponding hydroxy-acid, first noticed in the case of pilocarpine and pilocarpic acid by Marshall (*loc. cit.*), is shown in all the tropeines examined, and it seems hardly open to question but that this difference possesses important physiological significance, and further inquiry into the reason of this difference should throw considerable light on the mode of action of these substances.

EXPERIMENTAL.

Lactone of o-*Carboxyphenylglyceryltropeine,*



This base was prepared by passing hydrogen chloride through a solution of tropeine neutralised with the lactone of *o*-carboxyphenylglyceric acid, and maintained at a temperature of 120—125° for two to three hours (Täuber, D.R.-P. 95853). The resulting dark brown gum was decomposed by ammonia, and the base, which separated in grey crystals, was purified by recrystallisation from absolute alcohol and obtained in rosettes of stout, acicular, colourless crystals which melted at 172—173°. The base is insoluble in water and moderately soluble in alcohol :

0·2522 gave 0·6029 CO_2 and 0·1463 H_2O. $C = 65{\cdot}2$; $H = 6{\cdot}4$.

$C_{18}H_{21}O_5N$ requires $C = 65{\cdot}2$; $H = 6{\cdot}4$ per cent.

The *hydrochloride* separated from its aqueous solution, on evaporation in a vacuum over sulphuric acid, as a viscid oil which gradually solidified, forming dense rosettes of fine, acicular crystals. After recrystallisation from absolute alcohol, it was obtained in imperfect crystals, which melted at 228—229° and decomposed at 235°. This salt is anhydrous and is very easily soluble in water, but moderately so in absolute alcohol :

0·12 gave 0·0487 AgCl. $Cl = 10{\cdot}0$.

$C_{18}H_{21}O_5N,HCl$ requires $Cl = 9{\cdot}6$ per cent.

The *hydrobromide* separated from absolute alcohol in rosettes of fine, acicular crystals which melted at 212—213°; it is very easily soluble in water and moderately so in absolute alcohol. The air-dried salt contained 1 molecule of water of crystallisation, which was not entirely lost after five hours' heating at 150°, and at a higher temperature the substance decomposed :

0·2078 air-dried salt gave 0·0906 AgBr. $Br = 18{\cdot}6$.

0·1196 ,, ,, ,, ,, 0·0518 AgBr. $Br = 18{\cdot}4$.

$C_{18}H_{21}O_5N,HBr,H_2O$ requires $Br = 18{\cdot}6$ per cent.

The *hydriodide* crystallised from absolute alcohol in microscopic prisms which melted at 204—205°; it is anhydrous and is very easily soluble in water, but sparingly so in absolute alcohol:

0·1812 gave 0·0916 AgI. I = 27·3.

$C_{18}H_{21}O_5N,HI$ requires I = 27·6 per cent.

The *nitrate* crystallised from absolute alcohol in long, fine needles which melted at 174—175°. This salt is anhydrous and is very easily soluble in water and moderately so in alcohol:

0·0732 gave 0·1470 CO_2 and 0·0384 H_2O. C = 54·8; H = 5·8.

$C_{18}H_{21}O_5N,HNO_3$ requires C = 54·8; H = 5·6 per cent.

When this salt is heated for some time at 130° it decomposes, turning brown and losing water, and the decomposition product yields on recrystallisation from alcohol the nitrate of *iso*coumarincarboxyltropeine melting at 238°.

The *aurichloride* separated from boiling water in stellate clusters of yellow needles which melted at 215—216°; it is anhydrous and is moderately soluble in boiling water, sparingly so in alcohol:

0·3366 gave 0·0991 Au. Au = 29·4.

$C_{18}H_{21}O_5N,HAuCl_4$ requires Au = 29·4 per cent.

The *platinichloride* separated from boiling dilute hydrochloric acid in groups of stout, yellow needles which melted and decomposed at 193—194°. The air-dried salt contains 2 molecules of water of crystallisation which are only expelled at a temperature of 150°; the anhydrous salt is redder than the hydrated salt:

0·2026 air-dried salt lost 0·0063 H_2O. H_2O = 3·1.
0·1448 „ „ „ gave 0·0254 Pt. Pt = 17·5.
0·2902 „ „ „ „ 0·0509 Pt. Pt = 17·5.

$(C_{18}H_{21}O_5N)_2,H_2PtCl_6,2H_2O$ requires H_2O = 3·3; Pt = 17·6 per cent.

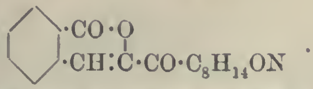
The *picrate* crystallised from hot water in short, yellow needles which melted at 218—220°.

The *methobromide* was prepared by adding excess of methyl bromide to a solution of the base in absolute alcohol at 0°, and allowing to stand for one hour, when it separated in small needles. After crystallisation from absolute alcohol it melted at 257—258°; this salt is readily soluble in water and very sparingly so in absolute alcohol:

0·17 gave 0·0756 AgBr. Br = 18·9.

$C_{18}H_{21}O_5N,CH_3Br$ requires Br = 18·8 per cent.

iso*Coumarincarboxyltropeine*,



This base was prepared by heating the lactone of *o*-carboxyphenylglyceryltropeine to 120—125° until no further diminution in weight took place. The product was somewhat discoloured, and was purified by repeated crystallisation from absolute alcohol; the pure base formed colourless, glistening leaflets melting at 179—180°, which are only sparingly soluble in water, ether, and cold alcohol:

0·1804 gave 0·4561 CO_2 and 0·1025 H_2O. C = 69·0; H = 6·3.
0·2100 „ 0·5315 CO_2 „ 0·1185 H_2O. C = 69·0; H = 6·3.
$C_{18}H_{19}O_4N$ requires C = 69·0; H = 6·1 per cent.

The *hydrochloride* separated from its solution in absolute alcohol in tufts of slender needles; it melted and decomposed at 287—288°, and is easily soluble in water, but sparingly so in boiling absolute alcohol. The salt is anhydrous:

0·2204 gave 0·0910 AgCl. Cl = 10·2.
$C_{18}H_{19}O_4N,HCl$ requires Cl = 10·1 per cent.

The *hydrobromide*, which separated from its solution in absolute alcohol in long, fine, matted needles, melted and decomposed at 252—253°; this salt is easily soluble in water and moderately so in absolute alcohol, and contains one-half a molecular proportion of water of crystallisation:

0·2811, dried at 100°, lost 0·0071 H_2O at 120°. H_2O = 2·5.
0·1016 „ „ 120°, gave 0·0494 AgBr. Br = 20·7.
$(C_{18}H_{19}O_4N,HBr)_2,H_2O$ requires H_2O = 2·2 per cent.
$C_{18}H_{19}O_4N,HBr$ requires Br = 20·3 per cent.

The *hydriodide* formed glistening scales which melted at 280—281°; it is sparingly soluble in water and absolute alcohol, and contains one molecule of water of crystallisation:

0·3616 air-dried salt lost 0·0139 H_2O at 150°. H_2O = 3·8.
0·2264 dried at 150° gave 0·1208 AgI. I = 28·8.
$C_{18}H_{19}O_4N,HI,H_2O$ requires H_2O = 3·9 per cent.
$C_{18}H_{19}O_4N,HI$ „ I = 28·8 „

The *nitrate* was precipitated as a flocculent mass of glistening needles on adding dilute nitric acid to the solution of the base in absolute alcohol; the salt melted and decomposed at 228—229°, and is readily soluble in water and sparingly so in absolute alcohol, but insoluble in ether. It contains one-half a molecular proportion of water of crystallisation, and after drying at 100°:

0·4677 lost 0·0111 H_2O at 120°. H_2O = 2·4.
0·1759 gave 0·3626 CO_2 and 0·0908 H_2O. C = 56·2; H = 5·7.
0·2015 „ 0·4125 CO_2 „ 0·1012 H_2O. C = 55·8; H = 5·6.
$(C_{18}H_{20}O_7N_2)_2,H_2O$ requires H_2O = 2·3; C = 56·1; H = 5·5 per cent.

The *aurichloride* was obtained as a yellow, crystalline precipitate; on recrystallisation from absolute alcohol it separated in imperfect crystals which melted and decomposed at 254—256°; the salt is almost insoluble in water and very sparingly soluble in boiling absolute alcohol; it is anhydrous:

0·1096 gave 0·0334 Au. Au = 30·5.

$C_{18}H_{19}O_4N,HAuCl_4$ requires Au = 30·2 per cent.

The *platinichloride* separated as a flocculent, amorphous precipitate. It was recrystallised from dilute hydrochloric acid and melted and decomposed at 264—265°. The salt is almost insoluble in water and alcohol, and contains 1 molecule of water of crystallisation, which is lost at 120°:

0·1802 lost 0·0031 H_2O. H_2O = 1·7.

0·1771, dried at 120°, gave 0·0329 Pt. Pt = 18·6.

$(C_{18}H_{19}O_4N)_2,H_2PtCl_6,H_2O$ requires H_2O = 1·7 per cent.

$(C_{18}H_{19}O_4N)_2,H_2PtCl_6$ requires Pt = 18·8 per cent.

The *picrate* crystallised from strong alcohol in matted, yellow needles, which turned brown at 240°, and melted and decomposed at 265°.

The *methobromide* was prepared in the same way as the lactone of *o*-carboxyphenylglyceryltropeine methobromide. It separated from absolute alcohol, in which it is sparingly soluble, in matted needles; it is readily soluble in water:

0·1168 gave 0·0542 AgBr. Br = 19·7.

$C_{18}H_{19}O_4N,CH_3Br$ requires Br = 19·6 per cent.

Homatropine Ethobromide, $C_{16}H_{21}O_3N,C_2H_5Br$.

This salt was prepared by heating homatropine with excess of ethyl bromide in a sealed glass tube at 100° for one hour, and was purified by crystallisation from absolute alcohol; it melted at 209—210°, and is readily soluble in water and moderately so in absolute alcohol, but insoluble in ether; it is anhydrous:

0·2138 gave 0·1028 AgBr. Br = 20·5.

$C_{16}H_{21}O_3N,C_2H_5Br$ requires Br = 20·8 per cent.

Homatropine methobromide, $C_{16}H_{21}O_3N,CH_3Br$, has already been prepared by Merck (D.R.-P. 145996), who gives the melting point 180—181°. On repeated recrystallisation from absolute alcohol, we have been able to obtain the salt in a state of greater purity. The pure salt melts at 192—196°, is very readily soluble in water, and moderately so in absolute alcohol; it is anhydrous:

0·2614 gave 0·1296 AgBr. Br = 21·1.

$C_{16}H_{21}O_3N,CH_3Br$ requires Br = 21·6 per cent.

Homatropine Methosulphate, $(C_{16}H_{21}O_3N)_2,(CH_3)_2SO_4$.

This salt was prepared by heating an alcoholic solution of homatropine with dimethyl sulphate in a sealed glass tube at 100° for two hours. On concentrating the alcoholic solution in a vacuous desiccator over sulphuric acid, a syrup was obtained from which a small quantity of crystals separated. After recrystallisation from absolute alcohol, the salt melted at 172—174°; it is readily soluble in water and moderately so in absolute alcohol:

0·1582 gave 0·0563 $BaSO_4$. S = 4·9.

$(C_{16}H_{21}O_3N)_2,(CH_3)_2SO_4$ requires S = 4·7 per cent.

Homatropine Methonitrate, $C_{16}H_{21}O_3N,CH_3{\cdot}NO_3$.

This salt was prepared by the action of silver nitrate on an aqueous solution of homatropine methobromide. The silver bromide was removed by filtration, and the filtrate evaporated in a vacuum, first on the water-bath, then in a desiccator over sulphuric acid. It separated as a viscid oil, which gradually solidified, and after crystallisation from absolute alcohol melted at 134—135°:

0·1875 gave 0·3963 CO_2 and 0·1183 H_2O. C = 57·6; H = 7·0.

$C_{16}H_{21}O_3N,CH_3{\cdot}NO_3$ requires C = 57·9; H = 6·9 per cent.

Tropine Methonitrate.

This was obtained in an attempt to prepare homatropine methonitrate by heating together homatropine and methyl nitrate in methyl alcoholic solution for two hours in a sealed tube at 100°. The clear solution was evaporated in a vacuum over sulphuric acid, and gave a viscid oil from which a small quantity of crystals separated. These crystallised from absolute alcohol in large, transparent cubes which began to turn brown at 280°, but did not melt at 300°:

0·2198 gave 0·3982 CO_2 and 0·1632 H_2O. C = 49·4; H = 8·3.

$C_8H_{15}ON,CH_3{\cdot}NO_3$ requires C = 49·5; H = 8·3 per cent.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

IX.—4-*Hydroxyphthalic and* 4-*Methoxyphthalic Acids.*

By WILLIAM HENRY BENTLEY and CHARLES WEIZMANN.

IN connexion with some experiments which we have conducted on derivatives of naphthacenequinone and rhodamines, we had occasion to prepare considerable quantities of 4-hydroxyphthalic acid which was first investigated by Baeyer (*Ber.*, 1877, **10**, 1079), who prepared it from 4-aminophthalic acid. According to Baeyer, the acid is obtained quite pure by dissolving the sublimed anhydride in water and allowing to crystallise; he gives 180° (about) as the melting point of the pure acid and 165—166° for the anhydride.

Graebe (*Ber.*, 1885, **18**, 1130), who prepared 4-hydroxyphthalic acid by fusing 4-sulphophthalic acid with caustic soda, found 180—183° for the melting point of the acid, and his analysis shows more carbon and hydrogen than corresponds to hydroxyphthalic acid, indicating at once that the material was not pure, whereas Baeyer's analytical data for the acid on the contrary give no such indication.

In order to prepare 4-hydroxyphthalic acid, we fused sulphophthalic acid with caustic soda (Graebe, *loc. cit.*; Rée, *Annalen*, 1886, **233**, 232), and greatly to our surprise obtained an acid having all the properties ascribed to 4-hydroxyphthalic acid and giving good figures on analysis, but melting at 204—205° and yielding an anhydride melting at 171—173°. In several subsequent experiments we obtained an acid melting at about 180°, which, after repeated crystallisations from water, melted at 186—187°; the mother liquors, however, on concentration yielded the acid melting at 204—205°. The acid melting at 186—187° had also the properties ascribed to 4-hydroxyphthalic acid, but analysis, as well as the fact that its anhydride melted indefinitely between 150° and 170° even after being twice crystallised, proved it to be impure.

As we considered the subject of considerable importance we endeavoured to discover the nature of the impurity in the acid melting at 186—187°, and with this object prepared the imide, anil, and dimethyl ester from each acid. These derivatives from the acid of higher melting point (204—205°) were easily obtained pure, but from the other acid (m. p. 186—187°) repeated crystallisation was always necessary, and, finally, the derivatives obtained from each acid were found to be identical. Moreover, the dimethyl ester from the acid of lower melting point yielded, on hydrolysis with alcoholic potash, the acid melting at the higher temperature. For some time we were unable to discover the nature of the impurity in the acid melting at 186—187°, but when we endeavoured to prepare pure 4-methoxyphthalic acid from each acid the results were so strikingly different that the impurity in the former was soon ascertained. 4-Methoxyphthalic acid, prepared from hydroxy-acid of higher melting point, was found to melt at about 170° with the formation of the anhydride melting at 98—99° (Schall, *Ber.*, 1879, **12**, 829, gives 138—144° and 93° respectively). When similar experiments were made with the acid of lower melting point, the product first melted at about 140° (see Schall, *loc. cit.*), and on crystallising from water yielded an acid melting at 108—109°, which on analysis gave numbers agreeing with methoxybenzoic acid, and which yielded *m*-hydroxybenzoic acid (m. p. 209°) on fusion with caustic potash. The impurity therefore in the acid in question and probably in samples of crude 4-hydroxyphthalic acid obtained by previous investigators is *m*-hydroxybenzoic acid. Subsequent experiments showed that when the fusion of 4-sulphophthalic acid with alkalis is prolonged or the temperature is too high, *m*-hydroxybenzoic acid is always produced, and the crude 4-hydroxyphthalic acid then always melts at about 180°. When, however, the fusion is carefully conducted, the formation of *m*-hydroxybenzoic acid is avoided, and the 4-hydroxyphthalic acid obtained always melts directly at about 200°. Graebe and Rée (*loc. cit.*) pointed out that *m*-hydroxybenzoic acid is sometimes found mixed with the hydroxyphthalic acid produced by their fusion of sulphophthalic acid, but the material which they considered to be pure 4-hydroxyphthalic acid must have still contained *m*-hydroxybenzoic acid.

EXPERIMENTAL.

Sulphonation of Phthalic Anhydride.

In a sealed tube or in the autoclave, phthalic anhydride is almost quantitatively sulphonated by heating with fuming sulphuric acid to 200°. In our experiments we employed a copper autoclave in which a porcelain pot, containing a mixture of phthalic anhydride (300 grams) and fuming (73 per cent. SO_3) sulphuric acid (500 grams), was placed. The autoclave was closed and heated to 200° for two to three hours; after cooling, the product, which consisted of a viscid syrup, was poured into water and neutralised with milk of lime. The soluble calcium salt was extracted with hot water and converted into the sodium salt, the solution of which was then evaporated until crystallisation commenced.

4-*Hydroxyphthalic Acid.*—As soon as the sodium salt of sulphophthalic acid commenced to crystallise it was transferred to a large nickel vessel or to the autoclave, carefully mixed with powdered caustic soda (1200 grams) and heated to 175—180° for three hours. The fused mass was then poured into a large dish, diluted with water, and acidified with hydrochloric acid. When the product contained *m*-hydroxybenzoic acid, this separated at once as a white precipitate while the liquid was hot, and the filtrate, on cooling, deposited a portion of the 4-hydroxyphthalic acid. After separating the latter, the liquid was extracted with ether, when a further portion of 4-hydroxyphthalic acid was obtained. The whole of the acid was then purified by crystallising from water, when, if the fusion had been conducted properly, it was obtained in warty masses melting at 204—205°. If the treatment with caustic soda had been too severe, the acid which separated after crystallising from water was found to melt at about 180°, but by evaporating the mother liquors further quantities of 4-hydroxyphthalic acid were obtained almost pure and melting at about 200°.

4-Hydroxyphthalic acid is sparingly soluble in cold water, easily so in the hot solvent; it dissolves readily in acetone, alcohol, or ether, but is almost insoluble in benzene or light petroleum. It melts at 204—205° with elimination of water and formation of the anhydride:

0·1410 gave 0·2714 CO_2 and 0·0427 H_2O. C = 52·49; H = 3·36.
$C_8H_6O_5$ requires C = 52·7; H = 3·3 per cent.

4-*Hydroxyphthalic Anhydride*.—The foregoing acid was fused and the heating continued until all effervescence had ceased. On crystallisation from glacial acetic acid, the anhydride separated in ill-defined needles melting at 171—173°:

0·1237 gave 0·2644 and 0·0281 H_2O. C = 58·3; H = 2·5.
$C_8H_{14}O_4$ requires C = 58·5; H = 2·4 per cent.

It is almost insoluble in cold water but readily soluble in the hot solvent, and the solution on cooling deposits the free acid. It dissolves readily in alcohol or acetone; in boiling toluene it is only sparingly soluble.

4-*Hydroxyphthalimide*.—This was prepared by heating the anhydride in a stream of dry ammonia and crystallising the product from alcohol. It separates in prismatic needles melting at 290° [Rée gives 288—289° (*loc. cit.*)]:

0·3213 gave 24·5 c.c. nitrogen at 20° and 756 mm. N = 8·7.
$C_8H_5O_3N$ requires N = 8·6 per cent.

4-*Hydroxyphthalimide* is soluble in boiling acetone, but only very sparingly so in boiling toluene.

4-*Hydroxyphthalanilic Acid*, $CO_2H{\cdot}C_6H_3(OH){\cdot}CO{\cdot}NH{\cdot}C_6H_5$.—This acid was prepared by dissolving 4-hydroxyphthalic anhydride (5·5 grams) in acetone and adding aniline (3·1 grams). The mixture became warm and, after evaporating the acetone, the residue was ground to a powder and extracted with cold aqueous sodium carbonate. From the filtered solution the *anilic acid* was precipitated by the addition of acetic acid, and purified by crystallising from alcohol; it separates in pale yellow leaves:

0·1840 gave 9·1 c.c. nitrogen at 17° and 756 mm. N = 5·7.
$C_{14}H_{11}O_4N$ requires N = 5·4 per cent.

The substance dissolves in cold aqueous sodium carbonate with a pale yellow colour which disappears when the solution is boiled. This is due to hydrolysis of the anilic acid, since the latter is not precipitated from the solution on acidifying with acetic acid. The anilic acid appears to melt at about 260°, but it is converted into the anil at a much lower temperature, and the melting point observed is really that of the latter.

4-*Hydroxyphthalanil*, $C_6H_3(OH)(CO)_2{:}N{\cdot}C_6H_5$.—This substance was prepared by heating the anilic acid until it melted and then crystallising the residue from alcohol, from which the *anil* was obtained in yellow leaves melting at 263—264°:

0·2432 gave 12·2 c.c. nitrogen at 15° and 764 mm. N = 5·9.
$C_{14}H_9O_3N$ requires N = 5·8 per cent.

It is almost insoluble in cold sodium carbonate solution, but dissolves with hydrolysis on boiling. It dissolves in cold dilute caustic soda, giving a yellow solution which yields the anilic acid. This can be precipitated with acetic acid and is apparently identical with the anilic acid just described. When dissolved in an excess of cold aqueous caustic soda the anil is completely hydrolysed, the yellow colour of the solution disappearing at the same time.

Methyl 4-Hydroxyphthalate, $C_6H_3(OH)(CO_2Me)_2$.—4-Hydroxyphthalic acid is esterified very readily when treated with methyl alcohol and sulphuric acid. The acid (30 grams) was dissolved in methyl alcohol (150 c.c.), mixed with concentrated sulphuric acid (100 c.c.), and warmed on the water-bath for a few hours. The cold product was poured into ice-cold water, the oil which separated extracted with ether, and the ethereal extract washed with a little sodium carbonate solution, dried, and evaporated. An oil remained which soon solidified, and after leaving in contact with porous porcelain until dry and crystallising from toluene, the methyl ester was obtained pure in minute plates melting at 107—108° [Rée, (*loc. cit.*), gives 102°].

The same substance was obtained from crude 4-hydroxyphthalic acid (m. p. 186—187°), but required several crystallisations before it was pure. On hydrolysis with alcoholic potash it then yielded 4-hydroxyphthalic acid melting at once at 204—205° (see p. 100):

0·1934 gave 0·4022 CO_2 and 0·0844 H_2O. C = 56·7 ; H = 4·8.
$C_{10}H_{10}O_5$ requires C = 57·1 ; H = 4·7 per cent.

Methyl 4-hydroxyphthalate is readily soluble in alcohol or ether, sparingly so in cold water, but more easily in the hot solvent or toluene; it dissolves readily in cold aqueous sodium carbonate, from which solution it can be extracted by ether. Owing to this property, a further quantity of the dimethyl ester was obtained when the extract, obtained by shaking the ethereal solution with sodium carbonate (see above), was acidified.

Methyl 4-Methoxyphthalate, $C_6H_3(OMe)(CO_2Me)_2$.—Pure 4-hydroxyphthalic acid (50 grams) was dissolved in aqueous caustic soda, and dimethyl sulphate (200 grams) added in small portions at a time, the mixture being constantly shaken and kept alkaline. At the end of the operation the product was heated for a short time on the water-bath, cooled, acidified, and extracted with ether. The ethereal solution was dried, evaporated, and the residue dissolved in methyl alcohol (250 c.c.), mixed with concentrated sulphuric acid

(160 c.c.), and heated a few hours on the water-bath. The cold product was then poured into ice-cold water, the oil which separated extracted with ether, the ethereal solution washed with dilute caustic soda, dried, and evaporated, when an oil remained which was purified by distillation under reduced pressure.

Methyl 4-methoxyphthalate is an oil which distils at 195—197°/20 mm. and does not solidify at $-10°$:

0·1466 gave 0·3144 CO_2 and 0·0712 H_2O. C = 58·5 ; H = 5·4.

$C_{11}H_{12}O_5$ requires C = 58·9 ; H = 5·3 per cent.

4-*Methoxyphthalic Acid*, $C_6H_3(OMe)(CO_2H)_2$.—This acid was prepared from the foregoing ester by hydrolysis with alcoholic potash on the water-bath; after diluting with water and evaporating until the alcohol had been removed, the solution was acidified with hydrochloric acid, when the acid was precipitated. It was collected and purified by recrystallising from water, from which it was obtained in glistening needles:

0·1110 gave 0·2233 CO_2 and 0·0411 H_2O. C = 54·9 ; H = 4·1.

$C_9H_8O_5$ requires C = 55·1 ; H = 4·1 per cent.

4-*Methoxyphthalic acid* is readily soluble in alcohol, acetone, or ether. When rapidly heated it melts at about 178° with effervescence. Slowly heated, it melts at about 170°.

As stated in the introduction, when we attempted to prepare 4-methoxyphthalic acid from the crude 4-hydroxyphthalic acid (m. p. 186—187°) we obtained first an acid melting at about 140° with effervescence, which on recrystallising from water melted at 108—109°, and proved on examination to be *m*-methoxybenzoic acid:

0·1137 gave 0·2620 CO_2 and 0·0533 H_2O. C = 62·8 ; H = 5·2.

$C_8H_8O_3$ requires C = 63·1 ; H = 5·3 per cent.

4-*Methoxyphthalic Anhydride*, $C_6H_3(OMe)(CO)_2O$.—This substance was prepared by heating the corresponding acid until it melted, and crystallising the product from glacial acetic acid, from which it separated in glistening leaflets melting at 98—99° [Schall (*Ber.*, 1879, **12**, 829) gives 93°]:

0·1182 gave 0·2625 CO_2 and 0·0363 H_2O. C = 60·6 ; H = 3·4.

$C_9H_6O_4$ requires C = 60·7 ; H = 3·4 per cent.

It is readily soluble in alcohol, acetone or warm benzene; in cold water it is almost insoluble, but melts in boiling water and gradually passes into solution, from which the free acid separates on cooling.

4-*Methoxyphthalimide*, $C_6H_3(OMe)(CO)_2NH$.—This imide was obtained by heating the anhydride in a stream of dry ammonia gas and crystallising the product from alcohol, when it separates in prismatic plates melting at 224—225°:

0·1711 gave 11·8 c.c. nitrogen at 16° and 764 mm. N = 8·08.

$C_9H_7O_3N$ requires N = 7·9 per cent

It is soluble in acetone, sparingly soluble in cold toluene, but more readily so in the boiling solvent.

4-*Methoxyphthalanilic Acid*, $C_6H_3(OMe)(CO_2H)CO{\cdot}NH{\cdot}C_6H_5$.—In order to prepare this derivative, the anhydride (10 grams) was dissolved in warm benzene and mixed with aniline (4·7 grams). The temperature of the mixture rose rapidly, and the *anilic acid* suddenly separated as a white, amorphous powder, which, after collecting by the aid of the pump and washing with benzene, was quite pure and melted at 148—149° with effervescence:

0·2727 gave 12·2 c.c. nitrogen at 17° and 764 mm. N = 5·2.

$C_{15}H_{13}O_4N$ requires N = 5·2.

It is readily soluble in alcohol or acetone and separates from dilute alcohol in leaflets.

4-*Methoxyphthalanil*, $C_6H_3(OMe)(CO)_2{:}N{\cdot}C_6H_5$.—This was prepared by heating the anilic acid at its melting point until effervescence had ceased. On crystallising the residue from alcohol, the anil separated in colourless needles melting at 179°:

0·2928 gave 13·8 c.c. nitrogen at 17° and 764 mm. N = 5·5.

$C_{15}H_{11}O_3N$ requires N = 5·5 per cent.

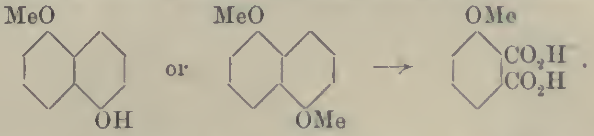
4-*Methoxyphthalanil* dissolves in hot dilute aqueous caustic soda, from which solution acetic acid precipitates an anilic acid. This, when purified by dissolving in sodium carbonate and reprecipitating with acetic acid, melts at 148—149°, and is probably identical with the anilic acid described above.

THE UNIVERSITY,
MANCHESTER.

X.—3-*Hydroxyphthalic and 3-Methoxyphthalic Acids and their Derivatives.*

By WILLIAM HENRY BENTLEY, RONA ROBINSON, and CHARLES WEIZMANN.

DURING the course of some experiments connected with the synthesis of *m*-hemipinic acid, it became necessary to prepare 3-methoxyphthalic acid. This acid had previously been prepared by Jacobsen (*Ber.*, 188, 16, 1965) by the oxidation of 6-methoxy-2-toluic acid with alkaline permanganate, but as 1 : 5-dihydroxynaphthalene is now comparatively easy to obtain in large quantities, it was considered that a simpler method of preparation of this acid would be the oxidation of the mono- or di-methyl ether of this substance:



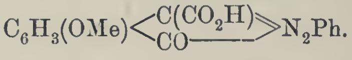
Considerable quantities of 3-methoxyphthalic acid and its anhydride were prepared in this manner, but the melting points of these substances were found to differ so widely from those given by Jacobsen (*loc. cit.*) that it was thought desirable to reinvestigate the whole subject and prepare some derivatives for the purpose of future identification. The results of this investigation, coupled with the fact that Jacobsen published no analytical data in his paper (*loc. cit.*), lead to the presumption that Jacobsen must have been dealing with impure materials, unless, indeed, the errors respecting the melting points are simply clerical.

In order to prepare 1 : 5-dihydroxynaphthalene, naphthalene was sulphonated in the cold with fuming sulphuric acid, and the sodium salt of the disulphonic acid was fused with caustic soda at 300°. The 1 : 5-dihydroxynaphthalene obtained in this way melted at 265°, which is a little higher than the melting point given in the literature.

1 : 5-Dihydroxynaphthalene is readily methylated by means of dimethyl sulphate and caustic soda, and yields the mono- and di-methyl ethers, which are easily separated owing to the solubility of the monomethyl ether in aqueous caustic soda. The dimethyl ether melts at 183—184°, and, on nitration in acetic acid solution, yields a mononitro-derivative melting at 165—166° and a dinitro-derivative melting at 270°.

The monomethyl ether melts at 140° and yields, on oxidation with permanganate in cold alkaline solution, three substances, namely (1) an acid of the empirical formula $C_{11}H_8O_4$ melting with decomposition above 200°, (2) methoxyphthalonic acid melting at 190—191°, (3) 3-methoxyphthalic acid melting at 173—174° (Jacobsen gives 160°) with formation of the anhydride. 3-Methoxyphthalic anhydride (but not the free acid) is also obtained by the oxidation of methoxyphthalonic acid in dilute sulphuric acid solution with cold permanganate, the anhydride separating as a white precipitate during the operation. This anhydride melts at 160—161° (Jacobsen gives 87°), and gives a fluorescein when heated with resorcinol. When the anhydride is treated in hot toluene solution with aniline, the corresponding *anilic acid* is precipitated, which melts at 164° with elimination of water and formation of the *anil* (m. p. 188·5—190°).

Heated in a stream of dry ammonia gas, 3-methoxyphthalic anhydride yields the *imide,* which sublimes in pale yellow needles and melts at 221—222°.

When methoxyphthalonic acid is heated with phenyl hydrazine, a condensation product is obtained, probably corresponding to that prepared by Henriques (*Ber.*, 1888, **21**, 1608) from phthalonic acid, namely, an anhydro-hydrazone,  $C_6H_3(OMe)<\begin{matrix}C(CO_2H)\\CO\text{———}\end{matrix}>N_2Ph$. It forms yellow needles melting at 186—188°.

From 3-methoxyphthalic acid, Jacobsen obtained 3-hydroxyphthalic acid by fusion with caustic potash. This acid had also been prepared from the corresponding sulphophthalic acid (Stokes, *Amer. Chem. J.* 1884, **6**, 282) and from aminophthalic acid (Bernthsen, Semper, *Ber.*, 1885, **18**, 167; 1887, **20**, 937).

Prepared by Jacobsen's method, 3-hydroxyphthalic acid was found to melt at about 150° with formation of the anhydride; the latter even after being twice recrystallised did not melt sharply, softening at 150°, and gradually melting as the thermometer rose to 190°.

Jacobsen gives 145—148° as the melting point of the anhydride, but remarks on the difficulty attending its purification.

3-Hydroxyphthalic anhydride, when treated in hot toluene solution with a molecular proportion of aniline, gives the *anilic acid* melting at 145° with evolution of gas and formation of 3-*hydroxyphthalanil*, which crystallises from dilute alcohol in short prisms and melts at 174—175°.

EXPERIMENTAL.

1:5-*Dihydroxynaphthalene.*

This was prepared in considerable quantities by adding the dry powdered sodium salt of naphthalene-1:5-disulphonic acid to two and a half times its weight of fused caustic soda (or potash) and gradually raising the temperature to 300° with constant stirring. The fused mass was dissolved in water, acidified with hydrochloric acid, and the 1:5-dihydroxynaphthalene crystallised from alcohol. It melts at 265°.

Methylation of 1:5-*Dihydroxynaphthalene.*—1:5-Dihydroxynaphthalene (160 grams) was dissolved in caustic soda solution, mixed with a little methyl alcohol, and treated alternately with small quantities of dimethyl sulphate and caustic soda solution, the whole being well shaken and cooled during the operation. When all the dimethyl sulphate (250 grams) had been added and sufficient caustic soda to render the liquor strongly alkaline, the product was heated on the water-bath for a short time, and afterwards diluted with water and filtered. The solid on the filter was well washed with water, dried and recrystallised several times from alcohol, from which it separated in white needles melting at 183—184°.

A quicker method of purification consists in distilling the crude brown substance from a retort at the ordinary pressure and then crystallising from alcohol.

0·1300 gave 0·3654 CO_2 and 0·0794 H_2O. C = 76·66 ; H = 6·78.

$C_{12}H_{12}O_2$ requires C = 76·59 ; H = 6·38 per cent.

1 : 5-*Dimethoxynaphthalene* is readily soluble in hot alcohol or glacial acetic acid, but only sparingly so in the cold solvents.

1 : 5-*Methoxynaphthol.*—The alkaline filtrate from the above solid contains the monomethyl ether, and in order to isolate this the liquor was acidified with hydrochloric acid, the brown precipitate collected, dried, and then distilled from a retort. The distillate was crystallised from glacial acetic acid, when the 1 : 5-methoxynaphthol separated in leaflets melting at 140°.

0·1135 gave 0·3171 CO_2 and 0·0575 H_2O. C = 76·21 ; H = 5·63.

$C_{11}H_{10}O_2$ requires C = 75·86 ; H = 5·75 per cent.

Mononitro-1 : 5-*dimethoxynaphthalene.*—This was prepared by dissolving 1 : 5-dimethoxynaphthalene (32 grams) in glacial acetic acid and gradually adding a mixture of nitric acid (18·2 grams, sp. gr. 1·42) and acetic acid, the liquid being kept well stirred and cooled during the addition. The product was then heated on the water-bath until all the crystals which separated out in the first instance had redissolved. On cooling, the nitro-compound separated, and was collected and crystallised from glacial acetic acid, from which it was obtained in yellow, rhombic plates melting at 165—166°.

0·1340 gave 7·5 c.c. nitrogen at 20° and 752 mm. N = 6·33.

$C_{12}H_{11}O_4N$ requires N = 6·01 per cent.

Nitrodimethoxynaphthalene is only sparingly soluble in acetic acid or toluene in the cold, but more readily so on warming. Reduced with zinc dust and acetic acid or with tin and hydrochloric acid, it yields a very dark-coloured substance which has the properties of an amino-compound, but was so difficult to purify that it was not further investigated.

Dinitro-1 : 5-*dimethoxynaphthalene.*—This substance was prepared in the same manner as the preceding one, with the exception that twice the quantity of nitric acid was employed. Purified by repeated crystallisation from acetone, it was obtained in pale orange-coloured prisms melting at 275°.

0·1350 gave 12·2 c.c. nitrogen at 20° and 752 mm. N = 10·22.

$C_{12}H_{10}O_6N_2$ requires N = 10·07 per cent.

Dinitro-1 : 5-*dimethoxynaphthalene* is very sparingly soluble in the usual organic solvents in the cold, and dissolves sparingly even in hot acetic acid or toluene, but it is more readily soluble in boiling acetone. Like the mononitro-derivative, when reduced with zinc dust and acetic acid it yields an amino-compound, which, however, is not easily purified, as it rapidly turns very dark in the air.

Oxidation of the Methyl Ethers of 1 : 5-*Dihydroxynaphthalene.*—1 : 5-Dimethoxynaphthalene is scarcely attacked by cold alkaline permanganate even after several days. When, however, the mixture is boiled for several hours, the permanganate is reduced, and small quantities of 3-methoxyphthalic acid can ultimately be extracted with ether from the acidified liquor. The yield is only small, and experiments showed that it is more advantageous to oxidise the mono-methyl ether, which is readily attacked by alkaline permanganate in the cold.

1 : 5-Methoxynaphthol (32 grams) was dissolved in a very dilute solution of caustic soda (7·5 grams), the solution was cooled by the addition of ice, and treated with a solution of potassium permanganate until the colour of the latter remained permanent for several minutes. During the addition, the liquid was strongly agitated and a current of carbon dioxide passed through it. At the end of the operation, the liquid was boiled and filtered from the manganese precipitate; the latter was extracted several times with boiling water and filtered. The united filtrates were nearly neutralised with hydrochloric acid, evaporated to a small bulk and acidified, when a small quantity of a light brown substance separated which was collected and dried. This substance is an acid which is very insoluble in most organic solvents; it dissolves in hot acetic acid, but does not appear to crystallise from it. It was purified by dissolving in sodium carbonate and precipitating again with acid; the precipitate was then collected, and dried first on porous plate and afterwards in a vacuum over sulphuric acid. When obtained in this way it is a light brown powder which melts above 200° apparently with decomposition, and yields on analysis numbers corresponding to the empirical formula $C_{11}H_8O_4$.

0·0988 gave 0·2324 CO_2 and 0·0358 H_2O. C = 64·15; H = 4·02.
0·1180 ,, 0·2770 CO_2 ,, 0·0420 H_2O. C = 64·01; H = 3·95.
$C_{11}H_8O_4$ requires C = 64·70; H = 3·92 per cent.

This new acid forms soluble salts with the alkalis and the alkaline earths. The barium salt was prepared by boiling the acid with water and barium carbonate for several hours, filtering and evaporating the filtrate to a small bulk, when the barium salt separated in brown plates. The salt was dried at 100°.

0·2165 gave 0·0861 $BaSO_4$. Ba = 23·38.
$C_{22}H_{14}O_8Ba$ requires Ba = 25·23 per cent.
$C_{22}H_{14}O_8Ba + 2H_2O$,, Ba = 23·66 ,,

The silver salt was prepared by adding silver nitrate to a neutral solution of the ammonium salt. A brown flocculent precipitate was obtained which was collected, washed well with hot water, dried on porous plate, and finally at 100°.

0·3135 gave 0·1014 Ag. Ag = 32·34.

$C_{11}H_7O_4Ag$ requires Ag = 34·72 per cent.

$C_{11}H_7O_4Ag + H_2O$ „ Ag = 32·85 „

The analytical data of the free acid and its barium and silver salts seem to point to the conclusion that the latter are salts of an acid of the empirical formula $C_{11}H_{10}O_5$, and that the free acid $C_{11}H_8O_4$ is a lactone derivative.

Henriques (*loc. cit.*), by the oxidation of α-naphthol with alkaline permanganate, obtained a similar insoluble acid corresponding to the empirical formula $C_{10}H_7O_4$, and which formed an easily soluble barium salt, $(C_{10}H_6O_4)_2Ba$.

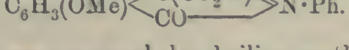
3-*Methoxyphthalonic Acid.*—After the separation of the acid just described, the aqueous liquors were extracted with ether, and the ethereal extract after evaporating deposited an oily acid from which, when placed in a desiccator over sulphuric acid, a solid very gradually separated. This was collected and purified by recrystallisation from a small quantity of water; it proved on analysis to be methoxyphthalonic acid.

0·1198 gave 0·2366 CO_2 and 0·0394 H_2O. C = 53·86; H = 3·65.

$C_{10}H_8O_6$ requires C = 53·57; H = 3·57 per cent.

3-*Methoxyphthalonic acid* is readily soluble in alcohol, ether, or water, and crystallises from the latter solvent extremely slowly in plates melting at 190—191°. Oxidised with potassium permanganate in acid solution it yields 3-methoxyphthalic anhydride.

Anhydrophenylhydrazone of Methoxyphthalonic Acid,



$$C_6H_3(OMe)<\genfrac{}{}{0pt}{}{C(CO_2H)}{CO\text{———}}>N\cdot Ph.$$

—This substance was prepared by boiling methoxyphthalonic acid in aqueous solution with phenyl hydrazine hydrochloride, filtering from some dark-coloured, oily substance, and evaporating the filtrate. A yellow solid separated, which was purified by dissolving in alcohol and precipitating with ether, when it was obtained in yellow needles melting at 186—188°.

0·0802 gave 6·8 c.c. nitrogen at 19° and 762 mm. N = 9·77.

$C_{16}H_{12}O_4N_2$ requires N = 9·46 per cent.

3-*Methoxyphthalic anhydride.*—The oily mother liquors from which the methoxyphthalonic acid had separated were distilled under reduced pressure and yielded a solid distillate which was purified by recrystallising from toluene, when 3-methoxyphthalic anhydride was obtained in prisms.

(1) 0·1326 gave 0·2928 CO_2 and 0·0424 H_2O. C = 60·22 ; H = 3·56.
(2) 0·1010 „ 0·2240 CO_2 „ 0·0324 H_2O. C = 60·48 ; H = 3·56.
$C_9H_6O_4$ requires C = 60·67 ; H = 3·37 per cent.

3-*Methoxyphthalic anhydride* melts at 160—161°, and when heated with resorcinol yields a fluorescein. It is almost insoluble in cold water, but dissolves somewhat slowly in hot water, from which after long standing the free acid separates.

3-*Methoxyphthalic acid*.—This acid was prepared from the anhydride by dissolving the latter in hot water and allowing the solution to evaporate in a desiccator over sulphuric acid. It separates in minute prisms melting at 173—174° with evolution of gas and formation of the anhydride. It is readily soluble in water, alcohol or ether.

0·1170 gave 0·2368 CO_2 and 0·0438 H_2O. C = 55·19 ; H = 4·15.
$C_9H_8O_5$ requires C = 55·10 ; H = 4·08 per cent.

The same acid was also prepared from methoxyphthalonic acid, which, as already stated, yields, on oxidation in cold acid solution with permanganate, 3-methoxyphthalic anhydride.

3-Methoxyphthalonic acid (1 gram) was dissolved in a small quantity of water, mixed with dilute sulphuric acid and cooled with ice to 0°. An ice-cold sulution of potassium permanganate (0·39 gram) was run in, and after a few minutes the permanganate became decolorised, carbon dioxide was evolved and a white precipitate separated. This was washed with a little water and dried; it then melted at 160°, and was evidently 3-methoxyphthalic anhydride. It dissolved slowly in hot water, from which solution on long standing in a desiccator over sulphuric acid crystals separated which melted at 174° and gave on analysis figures proving it to be 3-methoxyphthalic acid.

0·1122 gave 0·2270 CO_2 and 0·0403 H_2O. C = 55·17 ; H = 3·99.
$C_9H_8O_5$ requires C = 55·10 ; H = 4·08 per cent.

3-*Methoxyphthalimide*.—This substance was prepared by heating the anhydride in a stream of dry ammonia gas, when it sublimed in pale yellow needles. Crystallised from methyl alcohol, it was obtained in almost colourless needles melting at 221—222°.

0·1234 gave 8·5 c.c. nitrogen at 18° and 756 mm. N = 7·91.
$C_9H_7O_3N$ requires N = 7·91 per cent.

3-*Methoxyphthalanilic acid*, $C_6H_3(OMe)(CO_2H)CO\cdot NHPh$.—In order to prepare this derivative, 3-methoxyphthalic anhydride (1 gram) was dissolved in a small quantity of hot toluene and mixed with a solution of aniline (0·52 gram) in toluene. A white solid soon separated which was collected and recrystallised from dilute alcohol, when it separated in colourless plates melting at 164° with the formation of the anil.

0·1317 gave 6·2 c.c. nitrogen at 18° and 755 mm. N = 5·47.
$C_{15}H_{13}O_4N$ requires N = 5·16 per cent.

3-*Methoxyphthalanil*, $C_6H_3(OMe) < {\substack{CO \\ CO}} > NPh$.—The foregoing anilic acid melts at 164° with the evolution of gas, then solidifies and only melts again when the temperature of the bath reaches 180°. The product was purified by recrystallising from alcohol, from which it was obtained in colourless plates melting at 188·5—190°.

0·1618 gave 7·8 c.c. nitrogen at 20° and 764 mm. N = 5·54.
$C_{15}H_{11}O_3N$ requires N = 5·53 per cent.

3-*Hydroxyphthalic acid.*—This acid was prepared by fusing 3-methoxyphthalic acid with caustic potash.

The methoxy-acid (1 part) was added to strong caustic potash (10 parts) at 120°, when the temperature of the fusion immediately rose to 200°. After a few minutes, the product was dissolved in water, acidified strongly with hydrochloric acid and extracted repeatedly with ether. After evaporating the ether, an oily acid was obtained which probably consisted of a mixture of hydroxy- and methoxy-phthalic acids. In order to separate the hydroxyphthalic acid, the crude oily acid was esterified by warming on the water-bath with methyl alcohol and sulphuric acid for several hours. The cooled product was then poured into water, extracted with ether, the ethereal solution washed first with a solution of sodium carbonate and then with dilute caustic soda. The latter extract was acidified and again extracted with ether, when, after evaporating, a viscous oil was obtained which did not crystallise after standing two days. This oil was saponified with alcoholic potash and the resulting acid extracted with ether. The ethereal extract, after the removal of the ether, yielded again an oily acid, which, however, solidified when placed in a desiccator over sulphuric acid. The solid was pressed on porous porcelain and recrystallised from water, from which it separated, after long standing in a dessicator, in short prisms melting indefinitely at 150°, gas being evolved at 160°. As stated by Jacobsen, it yields a fluorescein with resorcinol and gives a cherry-red coloration with ferric chloride.

3-*Hydroxyphthalic Anhydride.*—3-Hydroxyphthalic acid readily loses water even at 100° with the formation of the anhydride. In order to prepare this substance, the acid was heated in a sulphuric acid bath until it melted and the evolution of gas had ceased. The residue was recrystallised twice from toluene, when the anhydride separated partly amorphous and partly in minute needles which melted indefinitely between 150° and 190°.

0·1055 gave 0·2258 CO_2 and 0·0260 H_2O. C = 58·30; H = 2·73.
$C_8H_4O_4$ requires C = 58·53; H = 2·44 per cent.

3-*Hydroxyphthalanilic Acid.*—This derivative was prepared in exactly the same manner as 3-methoxyphthalanilic acid (p. 110). It crystallises from dilute alcohol in long, slender needles melting at 145° with evolution of gas. Its alcoholic solution gives a reddish-brown coloration with ferric chloride.

3-*Hydroxyphthalanil.*—The anilic acid just described was heated in a sulphuric acid bath to 150°, and after crystallising the residue from dilute alcohol, the *anil* separated in short prisms melting at 174—175°.

0·0962 gave 4·8 c.c. nitrogen at 19° and 762 mm. N = 5·75.
$C_{14}H_9O_3N$ requires N = 5·85 per cent.

Like the anilic acid, the anil gives a reddish-brown coloration with ferric chloride.

CHEMICAL LABORATORIES,
UNIVERSITY OF MANCHESTER.

XI.—*A Relation between the Volumes of the Atoms of certain Organic Compounds at the Melting Point and their Valencies. Interpretation by Means of the Barlow-Pope Theory.*

By GERVAISE LE BAS, B.Sc.

IN October, 1905, the author discovered that the volumes of the atoms in certain members of the paraffin hydrocarbon series and their derivatives taken near their melting points and also in many solid compounds, both organic and inorganic, were very nearly integral multiples of the volume of combined hydrogen. In many cases these integral multiples coincide with the fundamental valencies of the atoms in question. This result, independently of its intrinsically interesting character, is at the present time especially significant in consequence of the ideas put forth by Barlow and Pope in their recent important paper on the correlation of molecular structure and crystalline form (Trans., 1906, **89**, 1675). By regarding crystalline structures as closely-packed assemblages built up from the spheres of influence of the constituent elements, these authors have arrived at the conclusion that the fundamental valency of an element is proportional within narrow limits to the volumes of the atomic spheres of influence.

It follows from this that a particular molecular complex may be regarded as one in which the component atoms appropriate to themselves portions of space proportional in volume to their valency, but, as, indeed, Barlow and Pope point out, the absolute volume, as the atomic sphere of influence of an element, is liable to differ from compound to compound.

It would seem, however, to follow, if no other determining factors than those promised by Barlow and Pope are operative, that the indicated relationship between the valency and the volume of the atomic sphere of influence should be traceable throughout a whole series of homologous substances such as the normal paraffins.

No obvious reason exists why the atomic sphere of influence of carbon or hydrogen should change appreciably in passing from one member to another of such a series, especially if the terms chosen lie so high in the series as to have nearly the same percentage composition.

This aspect of the new theory finds support from an examination of molecular volumes, taken under the specified conditions.

The data are derived from papers published by Krafft on the normal paraffins (*Ber.*, 1882, **15**, 1716) and on the alcohols (*Ber.*, 1883, **16**, 1714). The values quoted in the following table are for liquid hydrocarbons at the melting point; these temperatures are, as shown in the fifth column of the table, approximately equal fractions of the boiling points on the absolute scale, and hence may be considered as approximately equal fractions of the critical temperatures. The molecular volumes may thus be regarded as determined under corresponding conditions, that is, under conditions such that the repulsive forces in all cases have just overcome the attractive forces which hold them in their places in the crystalline structure.

Saturated Normal Hydrocarbons, C_nH_{2n+2}.

	W.	Mol. Vol. = *V*.	Diff. for CH_2.	M. p./B. p.	*V*/*W*.	*W* × *S* = Calc. mol. vol.
Undecane, $C_{11}H_{24}$ ………	68	201·4		0·527	2·962	201·96
Dodecane, $C_{12}H_{26}$ ………	74	219·9	18·5	0·536	2·971	219·78
Tridecane, $C_{13}H_{28}$ ………	80	237·3	17·4	0·524	2·966	237·60
Tetradecane, $C_{14}H_{30}$ ……	86	255·4	18·1	0·530	2·970	255·42
Pentadecane, $C_{15}H_{32}$ ……	92	273·2	17·8	0·520	2·970	273·24
Hexadecane, $C_{16}H_{34}$ ……	98	291·2	18·0	0·519	2·971	291·06
Heptadecane, $C_{17}H_{36}$, …	104	309·0	17·8	0·513	2·971	308·88
Octadecane, $C_{18}H_{38}$ ……	110	326·9	17·9	0·512	2·972	326·70
Nonadecane, $C_{19}H_{40}$ ……	116	344·7	17·8	0·506	2·971	344·52
Eicosane, $C_{20}H_{42}$…………	122	362·5	17·8		2·971	362·34
Heneicosane, $C_{21}H_{44}$ …..	128	380·3	17·8		2·971	380·16
Docosane, $C_{22}H_{46}$ … …..	134	398·3	18·0		2·972	398·00
Tricosane, $C_{23}H_{48}$ ………	140	416·2	17·9		2·971	415·80
Tetracosane, $C_{24}H_{50}$ ……	146	434·1	17·9		2·973	433·62
Heptacosane, $C_{27}H_{56}$ ……	164	487·4	53·3		2·972	487·08
Hentriacontane, $C_{31}H_{64}$…	188	558·4	71·0		2·970	558·36
Dotriacontane, $C_{32}H_{66}$ …	194	576·2	17·8		2·970	576·18
Pentatriacontane, $C_{35}H_{72}$.	212	629·5	53·3		2·969	629·64
Mean values	…………		17·83		2·970	

In the table, W is the valency number and the quotient V/W is the molecular volume divided by the valency number, thus representing the volume appropriated by one unit of valency in the respective hydrocarbon. The mean value of the latter, namely, $S = 2{\cdot}970$, is conveniently described as the unit stere. It is apparent at once, from the constancy of the individual values of S, that the concept above referred to, and which is of fundamental importance in Barlow and Pope's theory, can be extended to the statement that in the series of normal paraffins regarded under corresponding conditions specified the spheres of atomic influence of carbon and hydrogen preserve almost the same relative magnitudes throughout the series.

The extent to which this conclusion is true is measured by the closeness of the correspondence between the observed molecular volumes (column 3) and the values, calculated as the products of the valency volume and the mean value of the unit stere, in the last column.

The table shows that the mean increment of the molecular volume for the homologous increment CH_2 is 17·83, a value which, when divided by the valency volume $W = 6$, for methylene gives 2·972 for the value of the unit stere, a number almost identical with the mean value of S obtained from column 6.

A more direct way of calculating the value of the unit or univalent stere for hydrogen is by means of equations of the following kind :

$2S = 2V$ of $C_{12}H_{26}$ $- V$ of $C_{24}H_{58}$ $= 5{\cdot}7$. $S = 2{\cdot}85$.

$2S = (V$ of $C_{15}H_{32} + V$ of $C_{16}H_{34}) - V$ of $C_{31}H_{64} = 6$. $S = 3$.

The average value of S obtained in this way confirms that previously found, namely, 2·970.

The volume of carbon is also found directly as follows :

V of $C = 17{\cdot}83 - 5{\cdot}94 = 11{\cdot}89 = 4 \times 2{\cdot}972 = 4S$.

The conclusion is thus deduced that the molecular volume V (at the melting point) of a normal solid paraffin of the molecular composition C_nH_{2n+2} is given by the formula

$$V = (6n + 2)S = 6nS + 2S,$$

where $S = 2{\cdot}970$.

Considerations similar to the above may be applied to homologous series of derivatives of the normal paraffins, as, for instance, the primary alcohols. The following table gives the observed molecular volumes of several of these compounds examined by Krafft (*loc. cit.*).

Normal Alcohols, C_nH_{2n}·OH.

	W.	*V*.	*V/W*.	*W* × *S*.
Nonylcarbinol, $C_{10}H_{21}$·OH	64	188·3	2·943	190·08
Undecylcarbinol, $C_{12}H_{25}$·OH	76	223·9	2·946	225·72
Tridecylcarbinol, $C_{14}H_{29}$·OH	88	259·8	2·953	261·36
Pentadecylcarbinol, $C_{16}H_{33}$·OH	100	296·0	2·960	297·00
Heptadecylcarbinol, $C_{18}H_{37}$·OH	112	332·3	2·970	332·64

As against the slight divergence of *V/W* from the normal on the part of some of these alcohols, it has been found by a study of the ketones and fatty acids, in which latter series the hydroxyl group appears, that a satisfactory constancy is maintained.

Thus, under the stated conditions, the molecular volumes of the primary alcohols $C_nH_{2n+1}OH$ derived from the normal paraffins are expressed by the equation

$$V = (6n + 4)S = 6nS + 4S.$$

In a subsequent paper, the method of interpretation here described will be applied to other homologous series and also to unsaturated substances.

It is also the intention of the author to show that the regularities observed by Schröder in his study of solid compounds have underlying them relations similar to those given in this paper.

So far as the carbon compounds are concerned, it may be stated that Schröder's value for the stere is 5·95, or double the value which is here assigned to *S*, the unit stere.

Municipal School of Technology,
Manchester.

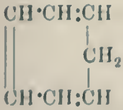
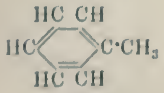
XII.—*The Optical Influence of Contiguity of Unsaturated Groups.*

By Julius Wilhelm Brühl.

The following remarks have reference to the striking physical properties of certain terpenes and their derivatives to which attention has been called recently by Kay and W. H. Perkin, jun. (Trans., 1906, **89**, 839) and are made with the object of correlating their results with those already obtained by myself and other inquirers.

The determinations of magnetic rotatory power made by Sir W. H. Perkin show that *d*-limonene (and inactive dipentene) differs in an altogether remarkable manner from $\Delta^{3.8(9)}$-*p*-menthadiene, the value obtained for the latter being "abnormally" high. The difference is ascribed by Kay and Perkin to the presence in the *p*-menthadiene of two contiguous ethenoid linkings. Now it can be shown not only that this explanation is a correct one, but also that it could have been foreseen with certainty that hydrocarbons so constituted would exhibit properties such as they are found to possess.

It is a well known fact that magnetic rotatory power and refractive and dispersive power are correlative properties; relations which demonstrably hold good between structure and refractive or dispersive power must, therefore, also obtain between structure and magnetic rotatory power. During the past sixteen years, indeed, I have shown by numerous researches,* carried out with a large body of material, that contiguous unsaturated groups, not only ·C⁚C·C⁚C· but also ·C⁚C·C⁚O, &c., always give rise to a striking increase of molecular refractive and still more of molecular dispersive power. I have often pointed out that the phenomenon is general, being observed not only in acyclic but also in the benzene, hydrobenzene and other series; moreover, that its existence affords a means, particularly in the case of terpenes and oxyterpenes (camphors), of determining whether or no contiguous unsaturated groups are present in a compound. Many Continental investigators have confirmed my conclusions, especially Eykman (J. F. Eykman, *Ber.*, 1889, **22**, 2736; 1890, **23**, 855; 1892, **25**, 3069), some of whose results are included in the following table, comprising a number of simple examples illustrative of the property under discussion:

$CH_3·CH:CH·CH:CH·CH_3$ …… *iso*Diallyl, b. p. 83°.	$\left(\frac{n^2_\alpha - 1}{n^2_\alpha + 2}\right)\frac{P}{d}$	29·87	$\left(\frac{n^2_\beta - 1}{n^2_\beta + 2}\right)\frac{P}{d}$	30·79	$M_\beta - M_\alpha$	0·92
$CH_2:CH·CH_2·CH_2·CH:CH_2$ … Diallyl, b. p. 61°.	,,	28·90	,,	29·57	,,	0·67
Theory for $C_6H_{10}\,|^{=}_{3}$ ………	,,	28·89				
 CH₂ …………………… Tropilidene.	,,	31·57	,,	32·57	,,	1·00
 ……………… Toluene.	,,	30·79	,,	31·63	,,	0·84
Theory for $C_7H_8\,|^{=}_{3}$ ………	,,	30·89				

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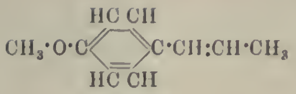
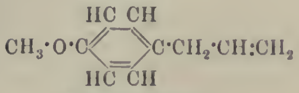
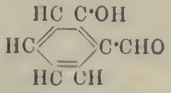
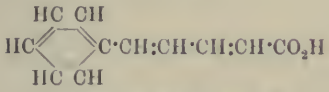
* My first observations on this subject are to be found in *Zeit. physikal. Chem.*, 1891, **7**, 140; my later work has been published partly in that periodical and also in the *J. pr. Chem.* and in the *Berichte*.

 Anethole.	$\left(\frac{n^2_\alpha-1}{n^2_\alpha+2}\right)\frac{P}{d}$	47·70	$\left(\frac{n^2_\gamma-1}{n^2_\gamma+2}\right)\frac{P}{d}$	50·65	$M_\gamma - M_\alpha$	2·95
 Methylchavicole.	,,	45·95	,,	47·99	,,	2·04
Theory for $C_{10}H_{12}O'$ $=_4$	,,	45·89			,,	1·75
CH_2:CH·CHO .... Acrolein.	,,	16·01			,,	0·73
Theory for C_3H_4O'' $\vert=_1$	,,	15·67			,,	0·58
.............. Salicylaldehyde.	,,	34·03			,,	2·68
Theory for $C_7H_6O'O''$ $=_3$	,,	32·52			,,	1·28
 Cinnamylideneacetic acid, dissolved in acetone.	,,	60·42			,,	9·70
Theory for $C_{11}H_{10}O'O''$ $=_5$	,,	50·06			,,	2·04

These few examples, which could easily be multiplied ten-fold, show that in every case the compound in which the unsaturated groups are contiguous has the greater molecular refractive and dispersive power, the experimental values in such cases always exceeding those calculated in the conventional manner; the differences, however, are not at all equal; they vary according to the character and number of unsaturated groups, being greatest and enormously in excess in the case of cinnamylideneacetic acid, in which there are several contiguous unsaturated groups.

It is remarkable that the benzene nucleus of toluene, which is a system of contiguous ethenoid linkings, does not behave optically as though it were thus constituted, the values it affords being normal, not in excess of those calculated (see table). Benzene and its homologues all behave alike; so do also benzene derivatives obtained by substituting univalent atoms for hydrogen: for example, bromobenzene, &c. What may be the cause of these seeming exceptions?

In benzenoid compounds, the closed ring consists of six equal carbon atoms forming three equally situated ethenoid groups which apparently neutralise one another. On this account, such compounds cannot exhibit the properties, chemical or physical, of ordinary contiguous (conjugated) ethenoid systems. As soon, however, as the equality of the six-carbon atoms is destroyed, the balance is disturbed; the properties characteristic of contiguous ethenoid linkings then at once make their appearance. The disturbance of balance may be effected in various ways.

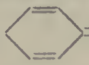
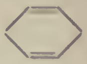
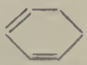
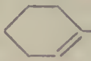
One method is to insert another atom or radicle between two of the six carbon atoms of the benzene nucleus, as in the case of tropilidene, which is formed by insertion of CH_2 into the benzene ring (see table).

A second method of destroying the equality of the carbon atoms in the benzene ring consists in associating one or more of these atoms with an unsaturated group, such as C⁚C, C⁚O, NO_2, NH_2, &c. These groups apparently exercise a special attractive influence on the nucleus and by conferring stability on the carbon atom with which they are combined disturb the balance within the ring. It is easy to show that such special attractive influences are actually at work. Thus allylbenzene, $Ph \cdot CH_2 \cdot CH{:}CH_2$, and all its derivatives are labile compounds which are easily convertible into propenylbenzene or cinnamene, $Ph \cdot CH{:}CH \cdot CH_3$, and its derivatives; the latter are stable and not reconvertible into their isomerides. Owing to the special attractive influence exercised by the ethenoid group C⁚C of the lateral chain upon the carbon atom of the benzene ring to which the group is attached, the carbon atom in the benzene ring acquires a particular quality and properties are developed which are characteristic of compounds containing contiguous ethenoid linkings; in fact, every known cinnamyl derivative (a large number have been examined) has a remarkably high refractive and dispersive power in comparison with that of the isomeric allylbenzene derivatives, none of which gives an abnormal value. Anethole, $C_6H_4(OCH_3) \cdot CH{:}CH \cdot CH_3$, and methylchavicole, $C_6H_4(OCH_3) \cdot CH_2 \cdot CH{:}CH_2$, are good instances (see table) of such differences.

It is to be supposed that two or more C⁚C linkings are attached to a benzene nucleus in naphthalene, phenanthrene and other condensed benzenoid hydrocarbons; these certainly are the cause of the exceptionally high refractive and dispersive power known to be characteristic of such hydrocarbons.

The aldehydes, acids and ethereal salts in which a carbonyl group C⁚O is attached to a benzene ring show a similar behaviour; for example, salicylaldehyde (see table), amino- and nitro-benzene and their derivatives. In the case of phthalic compounds, in which two CO groups are attached to the benzene nucleus, the increased optical effect is likewise remarkable. I have also drawn attention to the

increased optical effect manifest in derivatives of anthranilic acid, $C_6H_4<^{C(OH):O}_{NH_2}$, in a special investigation (*Ber.*, 1903, **36**, 3640).

A third method of destroying the equality in benzene consists in either removing one of the ethenoid linkings from the ring into the side chain or in dispensing with it altogether; by the former process; toluene, for example, would be changed into a compound having an increased optical effect, =CH$_2$ (I); whilst if the latter process were applied to benzene, one of the isomeric hydrobenzenes,  (II) or  (III), the prototypes of the terpenes, would be formed; of these, II would exercise a "normal" and III an increased optical effect. I have examined II myself (*J. pr. Chem.*, 1894, **49**, 248); III is unknown. Auwers (*Ber.*, 1906, **39**, 3748) has recently referred to the fact that not only compounds of types I and III but also those of the fourth type, –C:C (IV) all exhibit a remarkably increased refractive and dispersive power; he, however, expressly recognises that it was to be expected from my researches that compounds of these three types would be supra-refractive and supra-dispersive; I had indeed confidently expressed the opinion to him before he had carried out any of his determinations that such would turn out to be the case.

The discovery made by Sir W. H. Perkin that the $\Delta^{3\cdot 8\,9)}$-*p*-menthadienes (type IV) are more refractive and dispersive than limonene, in which there are no contiguous ethenoid linkings, serves to confirm the views which I have set forth in these pages. And considering the general correlation which exists between refractive and dispersive power and magnetic rotatory power, it was to be foreseen that limonene would exhibit normal and the $\Delta^{3\cdot 8(9)}$-*p*-menthadienes an increased magnetic rotatory power, although the extent of the difference could not have been predicted.

There is one other point of interest on which I may be allowed to add some remarks.

Sir W. H. Perkin has found that the magnetic rotatory power is slightly higher (13·061) in the case of optically active *d*-$\Delta^{3\cdot 8(9)}$-*p*-menthadiene than in that of the inactive *dl*-compound (12·939).* The values found for *d*- and *l*-limonene and dipentene were much lower, namely, 11·246, 11·162 and 11·315.

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* In the comparisons made by Kay and Perkin (p. 854), the same value is erroneously given to both compounds.

Comparing the optical properties generally of the various isomerides, it will be observed, on reference to Kay and Perkin's paper, that the values all follow the same order but that the differences between the refractive and dispersive powers, especially the latter, of *d*- and *dl*-$\Delta^{3.8(9)}$-*p*-methadiene are remarkably high in comparison with those between the magnetic rotatory powers. These differences are probably real, as they exceed the ordinary experimental errors.

Unfortunately the refractive and dispersive constants of *d*- and *l*-limonene were not measured by Sir W. H. Perkin. But judging from former determinations, there is no reason to suppose that appreciable differences exist in either refractive or dispersive power between *d*- and *l*-limonene and inactive dipentene. The last substance can be obtained by simply mixing *d*- with *l*-limonene and is probably merely an inactive mixture of optical antipodes. What then can be the reason that *d*-$\Delta^{3.8(9)}$-menthadiene and the *dl*- variety differ to such an extent in molecular refractive and still more in molecular dispersive power, whilst limonene and dipentene do not?

I think that it is not improbable that *dl*-$\Delta^{3.8(9)}$-*p*-menthadiene is not a mere inactive mixture but a racemic compound of the *d*- and *l*-antipodes. It is probable from Kay and Perkin's observations that *dl*-Δ^{1}-tetrahydro-*p*-toluic acid is not an inactive mixture but a racemic compound of the *d*- and *l*-components; it may well be that the hydrocarbon prepared from it by simple chemical transformations is also racemic.*

Of course, a conclusion of such consequence requires to be confirmed by further experiments, which, however, thanks to the progress in synthesis due to the researches of W. H. Perkin, jun., and his collaborators, will not offer great difficulties.

ADDENDUM.

In the above paper I mentioned that it was desirable to redetermine the spectrochemical constants of *d*- and *l*-limonene and of the inactive mixture of them (dipentene). By the kindness of Messrs. Schimmel and Co., I am now enabled to give these constants. This firm sent me *d*- and *l*-limonene which had been specially prepared for me with great care. *d*-Limonene was obtained from cumin oil (*Carum carvi*), *l*-limonene from the oil of the cones of the silver fir (*Abies pectinata*). Both terpenes were fractionated until the rotation remained constant. It was, however, not possible to obtain the two limonenes of quite equal rotatory power, that of *l*-limonene remaining a little lower. It seems, according to the opinion of Messrs. Schimmel and Co., that *l*-limonene is accompanied by some other constituent not separable by fractional distillation. This view was confirmed by the fact that a mixture of equal weights of *d*-limonene ($a_D + 104°15'$) and *l*-limonene ($a_D - 101°30'$), which have the same specific gravities ($d_4^{21} = 0·8402$ and $d_4^{20·5} = 0·8407$), does not display a rotatory power equal to the difference $+104°15' - 101°30' = +2°45'$, but that the rotation was actually found to be $+1°29'$, the mixture having again a practically unchanged specific gravity ($d_4^{20·85} = 0·8402$). As there is no other method of purifying the limonenes except by fractional distillation, the two samples prepared by Schimmel and Co. were used directly for my purpose. I am obliged to my colleague Prof. A. Klages and Mr. F. Sommer for making the measurements.

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* It must, however, be mentioned that the *dl*-hydrocarbon was prepared by eliminating water from the corresponding alcohol by boiling it with potassium hydrogen sulphate. It seems possible that, by this means, a partial inversion of the terpene generated might have taken place and that the special properties of this *dl*-terpene are perhaps due to such an alteration. This can only be decided by new physical determinations with a sample not treated with potassium hydrogen sulphate.

Four series of determinations were made: (1) on *d*-limonene, (2) on *l*-limonene, (3) on a mixture of equal weights of both, and (4) on a mixture obtained by adding to *d*-limonene so much of the *l*-compound that the deviation in the polarimeter became inappreciable.

Table.

I.	*d*-Limonene, b. p. (corr.) 175·5—176°/763 mm.	$a_D^{19·5°} = +104°15'$
II.	*l*-Limonene, b. p. (corr.) 175·5—176·5°/763 mm.	$a_D^{19·5°} = -101°30'$
III.	Mixture of equal weights of *d*- and *l*-limonene, b. p. (corr.) 175·5—176·5°/763 mm.	$a_D^{19°} = +\ 1°29'$
IV.	*l*-Limonene added to *d*-limonene until the mixture became inactive, b. p. (corr.) 175·5—176·5°/763 mm.	$a_D^{20°} = \pm\ 0°00'$

			n.			
	$t°$.	d_4^t.	H_α.	*D*.	H_β.	H_γ.
I.	21·0°	0·8402	1·47124	1·47428	1·48223	1·48886
II.	20·5	0·8407	1·47157	1·47468	1·48256	1·48924
III.	20·7	0·8409	1·47143	1·47448	1·48239	1·48904
IV.	20·85	0·8402	1·47134	1·47443	1·48231	1·48898

	$\frac{n^2-1}{(n^2+2)d}$.			
	H_α.	*D*.	H_β.	H_γ.
I.	0·3328	0·3347	0·3395	0·3434
II.	0·3328	0·3347	0·3394	0·3434
III.	0·3327	0·3345	0·3393	0·3433
IV.	0·3329	0·3348	0·3395	0·3435

	$\left(\frac{n^2-1}{n^2+2}\right)\frac{P}{d}$.				
	H^α.	*D*.	H_β.	H_γ.	$H\gamma - H^\alpha$.
I.	45·26	45·51	46·17	46·71	1·45
II.	45·26	45·52	46·16	46·71	1·45
III.	45·24	45·49	46·14	46·68	1·44
IV.	45·27	45·53	46·17	46·72	1·45
Theory for $C_{10}H_{16}\,|^{=}_{2}$	44·97	45·24	—	46·40	1·43

On reference to the table, it is seen that the agreement between *d*- and *l*-limonene is so excellent that the amount of heterogeneous constituents in *l*-limonene must be but very small. There is further a very close accordance between the theoretical values and those observed for the molecular refraction and an almost absolute agreement as regards molecular dispersion.

My numbers are also in satisfactory harmony with the figures given by Sir W. H. Perkin for dipentene; mine are a little higher for molecular refraction, and somewhat lower for molecular dispersion.

The main result of these determinations is the fact that *d*- and *l*-limonene and their inactive mixture (dipentene) display, except in rotatory power, almost absolutely equal constants in every respect: in boiling point, specific gravity, refractive indices for every wave-length, specific and molecular refractions and dispersions within the whole visible spectrum.

Since *d*- and *dl*-$\Delta^{3.8(9)}$-*p*-menthadiene, prepared by Kay and Perkin, show remarkable differences in these physical constants, it is obvious that their relation cannot be the same as that of *d*- and *l*-limonene on the one hand and dipentene on the other. Therefore *dl*-$\Delta^{3.8(9)}$-*p*-menthadiene is probably a racemic compound—if the properties are not altered during its preparation (boiling with potassium hydrogen sulphate). At present it seems more likely that the difference in the optical behaviour of this *dl*-compound is due to racemisation and not to chemical change (conversion into terpenes of another kind), as the magnetic rotation of *d*- and *dl*-$\Delta^{3.8(9)}$-*p*-menthadiene displays but slight differences. A decisive conclusion, however, in this very interesting question can only be arrived at by preparing the *dl*-compound avoiding treatment with potassium hydrogen sulphate and by redetermination of its physical properties.

HEIDELBERG.

XIII.—*The Action of Acid Chlorides on Thioureas.*

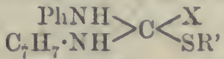
By AUGUSTUS EDWARD DIXON and JOHN HAWTHORNE.

IT is well known that alkylogens can unite with thiourea and with certain of its derivatives, in particular with those where univalent hydrocarbon radicles replace one, two, or three hydrogen atoms of the nitrogenised groups in $CS(NH_2)_2$ or $NH{:}C(SH)\cdot NH_2$.

Since, in the products, the alkyl, R, of the alkylogen, RX, is combined with the sulphur atom, the change, where a thiourea is concerned, may most simply be explained by supposing the hydrogen of the group to be substituted by the alkyl group, thus:

$$NH{:}C(NH_2){\cdot}SH + RX = NH{:}C(NH_2){\cdot}SR + HX.$$

Being highly basic, the products retain the acid, HX, which is eliminated by alkali, leaving the free base or *pseudo*thiourea isomeric with the ordinary thiourea containing the same radicle.

Where union is effected between an alkylogen and a thiocarbamide, for example, $PhNH{\cdot}CS{\cdot}NH(C_7H_7)$, a molecular change of the latter may be supposed to occur with formation of $PhN{:}C(NH{\cdot}C_7H_7){\cdot}SH$ (or its tautomeride), which then interacts as shown above. Probably an additive compound, such as  $\begin{matrix}PhNH\\C_7H_7{\cdot}NH\end{matrix}{>}C{<}\begin{matrix}X\\SR\end{matrix}$, is first formed, and a hydrogen atom then withdrawn (as HX) from the NH group.

If the sulphur atom is already combined with a hydrocarbon group, the free base (but not its salts) can unite with the radicle of an alkylogen; in this case the radicle attaches itself to a nitrogen atom (see, for example, Bertram, *Ber.*, 1892, **25**, 48).

Concerning the behaviour of acylogens with thioureas, our knowledge is very limited. So long ago as 1875, Claus described (*Ber.*, 1875, **8**, 42) a molecular compound CH_4N_2S,C_2H_3OCl, obtained by acting on thiourea with acetyl chloride below 40°; the product is said to dissolve unchanged in cold alcohol, but to decompose when the solution is heated, without formation of acetylthiourea. Benzoyl chloride, on the other hand, acts on thiourea to produce benzoylthiourea, but only at 120° (Pike, *Ber.*, 1873, **6**, 755). If, however, acetyl or benzoyl chloride is slowly added to a pyridine solution of thiocarbanilide, a monoacetyl or a dibenzoyl derivative is formed (Deninger, *Ber.*, 1895, **28**, 1322), in which, presumably, the acid group is directly attached to nitrogen.

More recently it has been shown (Trans., 1903, **83**, 565) that thiourea unites very readily with methyl or ethyl chlorocarbonate to form in each case an additive product, $CSN_2H_4,RO{\cdot}COCl$, the hydrochloride of a base, $NH_2{\cdot}C(NH){\cdot}S{\cdot}CO_2R$, and, moreover, that from monosubstituted thioureas similar compounds may be obtained; in so far as these products contain the acyl or oxidised group united with the sulphur, they are strictly analogous to the alkylogen derivatives already mentioned. Furthermore, it has been shown (Dixon, Trans. 1906, **89**, 909) that a similar combination occurs when thiourea is brought into contact with phenyl chlorocarbonate, $PhO{\cdot}COCl$, there being formed the hydrochloride of a base, $NH_2{\cdot}C(NH){\cdot}S{\cdot}CO_2Ph$, isomeric with a non-basic carbophenoxythiourea,

$$PhO{\cdot}CO{\cdot}NH{\cdot}C(NH){\cdot}SH,$$

described in the same paper.

Certain differences are noticeable amongst these *pseudo*derivatives;

for example, when the radicle, R, of the group, CO·OR, united with the sulphur atom, is fatty, the product readily loses carbon dioxide, and the radicle thereupon attaches itself directly to sulphur, forming an alkyl*pseudo*base, $NH_2{\cdot}C(NH){\cdot}S{\cdot}R$, whereas if this radicle is aromatic a phenol results, thus:

$$NH_2{\cdot}C(NH){\cdot}S{\cdot}CO_2Ph + H_2O = PhOH + CO_2 + NH_2{\cdot}C(NH){\cdot}SH.$$

In no case, however, where a chlorocarbonate was united to thiourea or to a monosubstituted thiourea did the radicle CO·OR, or any part of it, become attached to nitrogen.

The group $CH_3{\cdot}CO$ is of course more highly electronegative than the group $CH_3{\cdot}O{\cdot}CO$ and its congeners; nevertheless, in view of the above facts, a possible explanation of the phenomenon observed by Claus suggests itself, namely, that acetyl chloride may to some extent play the part of an alkylogen, its acetyl group becoming combined with the sulphur so as to yield the hydrochloride of a *pseudo*- or basic form:

$$NH_2{\cdot}C(NH){\cdot}SH + Cl{\cdot}CO{\cdot}CH_3 = NH_2{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}CH_3,HCl.$$

To throw light on the subject and to investigate the power of combination between acylogens and thioureas in general, the present inquiry was commenced. This is still incomplete, but circumstances having now arisen which will preclude us from continuing it jointly, we have the honour to lay before the Society an account of the principal results so far attained.

Acetyl Chloride and Thiourea.

As Claus gives scarcely any description of his compound (*loc. cit.*) beyond the statement that it is highly unstable, being decomposed at about 40°, yet dissolves unchanged in warm alcohol, it was necessary to re-examine the substance.

When finely powdered thiourea was covered with acetyl chloride, union occurred, with evolution of heat and formation of a bulky, lustrous, deliquescent white powder, apparently crystalline; this, however, was always more or less impure, as on determining the chlorine and sulphur respectively, figures were obtained corresponding to mixtures of additive compound and thiourea, in which the former was present to the extent of from 94 to 96 per cent. The only analytical figure given by Claus (*loc. cit.*) is that for chlorine, namely, 22·1 per cent., whilst CSN_2H_4,C_2H_3OCl requires $Cl = 22{\cdot}98$ per cent.; from this it would appear probable that he was dealing with a mixture containing 4 per cent. of thiourea and 96 per cent. of additive compound.

Attempts to combine thiourea, suspended in benzene, with acetyl chloride proved unsuccessful, but ultimately a pure product was obtained by adopting the following method. To a nearly saturated solution of thiourea in warm acetone, excess of acetyl chloride, diluted with the same solvent, was added gradually; the precipitate, consisting of minute, soft, pearly plates, was collected, washed thoroughly with acetone, and dried, first by exposure to warm air and finally in a vacuum desiccator. The yield amounted to more than 90 per cent. of the theoretical.

Prepared in this way, the compound was fairly stable; it was odourless when dry, and, although deliquescent, was not sufficiently so to preclude its being weighed in an open vessel for analysis. When heated in a narrow tube it melted sharply at 109° with copious effervescence.

Chlorine was determined by fusing a weighed quantity with pure caustic soda, and subsequently with nitre; the product, dissolved in water, was acidified by nitric acid and the mixture treated with excess of *N*/10 silver nitrate. After most of the nitrous acid had been expelled by boiling, the remainder was destroyed by urea, and the silver in solution determined by Volhardt's method, using *N*/10 ammonium thiocyanate. In all the chlorine determinations given later, except where it is otherwise stated, a similar method was adopted:

0·309 required 19·8 c.c. *N*/10 silver nitrate; Cl = 22·75.

$C_3H_7ON_2ClS$ requires Cl = 22·98 per cent.

The substance dissolved very freely in cold water, yielding an acid solution which remained clear on treatment with *N*/10 caustic alkali, of which two equivalents were required for saturation; no thiocyanate was present in the neutralised solution:

0·1545 required 19·95 c.c. *N*/10 NaOH; theory requires 20 c.c.

It was considerably less soluble in absolute alcohol, the solution, when warmed with sulphuric acid, developing the odour of ethyl acetate. The aqueous solution yielded with silver nitrate a white precipitate, blackened instantly on the addition of ammonia, and was readily desulphurised by heating with an alkaline solution of lead, with formation of a brilliant mirror of galena. Moreover, the aqueous solution, when evaporated to a small bulk, yielded thiourea, which melted at 171—172° and was identified by comparison with pure thiourea (m. p. 171—172°) and by the mixed melting point method.

The decomposition by water proceeds, therefore, as shown by the equation:

$$C_3H_7ON_2ClS + H_2O = HCl + CH_3{\cdot}CO_2H + NH_2{\cdot}C(NH){\cdot}SH.$$

Consistently with this, when the aqueous solution was treated in presence of dilute nitric acid with excess of *N*/10 silver nitrate, the precipitate collected, and the residual silver determined by Volhardt's method, it was found that two molecules of silver salt were absorbed for each molecule of hydrochloride taken; of these two molecules, one combined with the hydrochloric acid and the other formed the molecular additive compound $CSN_2H_4,AgNO_3$, described by Reynolds (Trans., 1892, 61, 251).

Claus' observations were so far confirmed, that in this decomposition by water no sign was detected of the formation of acetylthiourea; in other words, the acetyl group is not combined with a nitrogen atom. Another experiment, made by treating one molecular proportion of the hydrochloride, dissolved in anhydrous alcohol, with an alcoholic solution containing one equivalent of sodium, gave a similar result, sodium chloride being precipitated, and the filtrate, by concentration, yielding crystals of ordinary thiourea.

It does not follow, however, that the acetyl chloride is held merely by some attraction such as that whereby water of crystallisation is retained in certain compounds, for the fact that acetic acid as well as hydrochloric acid is formed on hydrolysis is equally consistent with the view that partition of the acetyl chloride occurs when it unites with thiourea, the chlorine becoming associated with hydrogen and the acetyl group attaching itself to the sulphur atom to form $NH_2\cdot C(NH)\cdot S\cdot CO\cdot CH_3$. Such a compound is basic in type, in the same sense as $NH_2\cdot C(NH)\cdot S\cdot C_2H_5$ and its congeners, and since the presence of an acetyl group in place of the electropositive alkyl must greatly weaken the basic character, it is quite to be expected that combined hydrogen chloride, if present, should exert towards alkali the same acidity as if it were free. In presence of water the combined acetyl group also displays full activity, as just shown, but considering that this group is eliminated by dilute alkali, even when united with nitrogen in *ab*-disubstituted thiocarbamides, it was to be expected that it would very readily be separated from sulphur, for which element (as may be noticed in the case of thiolacetic acid) its affinity is but feeble.*

Moreover, that the acylogen is not held as acetyl chloride of crystallisation seems probable from the behaviour of the compound on heating, for if at 109° the acylogen simply passed off, thiourea alone should be left, whereas it will be shown later that this is not the case. Furthermore, that hydrogen chloride is held as such, combined in the molecule, may be inferred from the fact that it is possible, as shown in the following experiment, to replace it by a different acid.

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* Acetylthiourea parts very readily with the acetyl group. Thus, when 1 molecule of the pure substance, dissolved in cold water, was mixed with excess (2 molecules) of *N*/10 alkali, and the solution allowed to stand for a certain time before titrating back with *N*/10 acid, we found that, after five minutes' standing, seven-tenths of 1 molecule of alkali had been absorbed and, after ten minutes, exactly 1 molecule.

To a concentrated aqueous solution of the acetyl compound, slight excess of a saturated aqueous solution of picric acid was slowly added; the resultant precipitate of minute, yellow, interlacing needles, when thoroughly washed with water and dried, melted sharply at 120°. Since the original compound is somewhat readily dissociated by water, with formation of thiourea (which gives no picrate), and the picrate itself does not escape hydrolysis, a poor yield was obtained. The product was free from chlorine; its aqueous solution, when treated with silver nitrate followed by ammonia, gave a black precipitate, and was readily desulphurised by heating with an alkaline solution of lead. That the acetyl group still remained in combination was shown by dissolving a portion in alcohol, acidifying with sulphuric acid, and warming, when the odour of ethyl acetate became distinct:

0·347 gave 0·2354 $BaSO_4$. S = 9·3.
0·3292 ,, 56·8 c.c. moist nitrogen at 14° and 753 mm. N = 20·2.
$C_9H_9O_9N_5S$ requires S = 9·22; N = 20·17 per cent.

Now, a solution of acetylthiourea in water yields no picrate with aqueous picric acid, it is somewhat sparingly soluble in cold water, and does not dissolve more readily in cold dilute hydrochloric acid; when picric acid is added to the solution in the latter, no precipitate is formed unless the hydrochloric acid is sufficiently concentrated, in which case picric acid itself crystallises out.

Accordingly, the above substance is the *picrate* of an acetyl-ψ-thiourea, $NH_2\cdot C(NH)\cdot S\cdot CO\cdot CH_3$, isomeric with the compound melting at 165°, obtained by Nencki (*Ber.*, 1873, **6**, 599) from thiourea and acetic anhydride, and by Doran (Trans., 1905, **87**, 341) from acetylthiocarbimide and ammonia.

Action of Heat.—A quantity was melted in a test tube immersed in a bath of sulphuric acid, the temperature of which was kept between 110° and 115°. The liquid bubbled freely, fumes of hydrogen chloride being evolved together with an odour recalling that of thioacetic acid; it then became brown, and soon began to solidify. After some twenty minutes the effervescence had almost ceased, when the now solid residue was withdrawn from the bath and twice crystallised from boiling water, being obtained in small, white needles free from chlorine and melting at 166° (corr.). It gave the usual thiocarbamidic reaction (desulphurisation) with hot alkaline solution of lead, and when heated with alcohol and dilute sulphuric acid developed the odour of ethyl acetate. A specimen of pure acetylthiourea, attached to the same thermometer, melted at the same temperature, and when approximately equal weights of the two substances were mixed, the melting point of the mixture was found to be unchanged; consequently the product was acetylthiourea.

From the results of these various observations, we conclude that in the additive compound of acetyl chloride with thiourea the acetyl group is united directly to sulphur, the resultant molecule being basic, not alone in type, but also to some extent in character, and that when heat is applied the acetyl group migrates to a nitrogen atom so as to yield ordinary acetylthiourea:

$$NH_2\cdot C(NH)\cdot S\cdot COMe,HCl = HCl + NH{:}C(NH\cdot COMe)\cdot SH.$$

It may be that this transference of the group named occurs as the primary effect of heat, in which case the resultant acetylthiourea, being for all purposes non-basic, could not retain the hydrogen chloride previously held by the molecule of more basic configuration and character; or possibly the hydrogen chloride, being feebly held by so weak a base, is parted readily from it by increase of temperature; if so, the wandering of the acetyl group from sulphur to nitrogen, for which it has much more affinity, might occur readily enough.

At present it is not easy to decide between these hypotheses, but in view of the observation previously mentioned, that withdrawal of the combined hydrogen chloride by means of a single equivalent of sodium ethoxide fails to produce acetylthiourea, there is at least some ground for believing that in this case the transfer of the acetyl group from sulphur to nitrogen is not conditioned independently of temperature.

The mechanism of this additive change being so far explained, we may now describe the results of experiments made with other thioureas and acylogens.

Acetyl Chloride and Phenylthiourea.

On mixing finely-divided phenylthiourea, suspended in benzene, with excess of acetyl chloride, union occurred immediately without material rise of temperature, the product, the yield of which amounted to 93 per cent. of the theoretical for a molecular additive compound, being apparently crystalline. The same compound, but in a state of higher purity, was obtained by adding considerable excess of acetyl chloride to a tepid, concentrated solution of the thiourea in acetone. On cooling this mixture, lustrous, white, flattened prisms were deposited; these were colourless when dry, and melted, if quickly heated, at 94° with copious effervescence. The melting point is dependent on the duration of heating, becoming markedly lower if this is prolonged:

0·2305 gave 0·2345 $BaSO_4$. S = 14·0.

0·2305 required 10·2 c.c. *N*/10 $AgNO_3$. Cl = 15·7.

$C_9H_{11}ON_2ClS$ requires S = 13·88; Cl = 15·40 per cent.

When treated with sulphuric acid the solid additive compound effervesced, evolving fumes of hydrogen chloride. It was freely soluble in cold water, yielding an acid solution, from which, if not too dilute, prismatic crystals of phenylthiourea separated; in the aqueous mother liquor both hydrochloric and acetic acids were present, but no thiocyanic acid.

It is plain that in the additive compound the acetyl group is not directly associated with nitrogen; otherwise acetylphenylthiocarbamide (either *aa*- or *ab*-) must be produced by hydrolysis on contact with water. The possibility of acetyl chloride being held in some sort of mechanical combination was negatived, just as in the case of the corresponding thiourea derivative, by the observation that the hydrochloric acid may be eliminated and a picrate of the "base" may be obtained.

Owing to the ready dissociation of the original compound by water, its aqueous solution must be combined quickly with the picric acid; otherwise little or no picrate is formed; moreover, the picrate itself, although tolerably stable when once obtained, is dissociated by much water if this is present when combination takes place. The *picrate* was obtained in minute, lemon-yellow needles, becoming highly electrical on friction; they were free from chlorine, almost insoluble in cold water (but dissociated by boiling with it), and melted to a deep bromine-coloured liquid at 187—188°, with previous darkening. The substance was decomposed by warming with caustic potash, and hence was desulphurised when heated with an alkaline solution of lead:

0·4113 absorbed 19·8 c.c. $N/10$ barium chloride. $S = 7·7$.

$C_{15}H_{13}O_8N_5S$ requires $S = 7·56$ per cent.

Ordinary substituted thioureas and thiocarbamides (that is, those in which the substituting radicles are attached to nitrogen) do not yield picrates readily, if at all. Thus, when *ab*-acetylphenylthiocarbamide, dissolved in acetone, was treated with an aqueous solution of picric acid, brilliant plates were deposited; these, however, became pearly white on washing, and proved on examination to be nothing more than the unaltered thiocarbamide, precipitated by the water used as solvent. Neither was it found possible to combine picric acid with *aa*-acetylphenylthiocarbamide, $AcPhN·CS·NH_2$, dissolved in alcohol, acetone, or water. In a further experiment, made by leading a large excess of dry hydrogen chloride through a nearly saturated solution of the *aa*-compound in cold acetone, no hydrochloride was precipitated, nor, after evaporating the solution to a pasty consistence and removing some oily product (having an odour of mercaptan) by washing slightly with alcohol, did the solid residue contain any chlorine; it consisted, in fact, of the original thiocarbamide, nearly pure.

Phenylthiourea, in water or alcohol, gave no picrate; moreover, when dry hydrogen chloride was led through its solution in acetone, no solid was produced; instead, hydrogen sulphide escaped, and the residual liquid had a strong odour of mercaptan. So far as may be judged from these experiments, it seems a justifiable conclusion that mono- and di-substituted thioureas or thiocarbamides are almost devoid of basic characters, but that a molecule having the configuration $NH{:}C(SH){\cdot}NH_2$ becomes basic when an organic radicle is substituted for the SH hydrogen, and does so independently of whether the substituting radicle is itself electropositive or electronegative, this character affecting merely the strength of the resultant base.

For the various reasons set forth above, we infer that the additive product of acetyl chloride and phenylthiourea is a definite chemical compound, namely, the hydrochloride of an acetylated phenylthiourea, in which the acetyl group is joined to the rest of the molecule through the sulphur atom; otherwise, iminoacetylthiolphenylcarbamic acid, or, according to the nomenclature suggested by one of us (Trans., 1895, 67, 564), acetyl-ψ-ν-phenylthiourea, $C_6H_5NH{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}CH_3$. This represents a typical basic form or *pseudo*thiourea, analogous to the known derivatives, having distinctly positive radicles attached to the sulphur atom. As a rule, members of the latter class are hydrolysed more or less readily by alkali, that is, as soon as the combined acid is withdrawn, but in such cases the sulphur atom passes off in combination with the alkyl group as mercaptan.

Action of Heat.—A quantity of the hydrochloride contained in a test-tube immersed in a bath of sulphuric acid was heated slightly above its melting point until the effervescence (due principally to the escape of hydrogen chloride) ceased; the liquid, which had an odour of thioacetic acid, now gradually solidified, and the residue, on crystallisation from boiling water, separated in glistening leaves melting at 170—171° and consisting of *ab*-acetylphenylthiocarbamide. Heat, therefore, just as in the case of the corresponding thiourea derivative, brings about a movement of the acetyl group from the sulphur to one of the nitrogen atoms, whilst the molecule changes in configuration from the iminothiocarbamic to the thiocarbamidic form.

Action of Alkali.—Attempts to neutralise the dilute aqueous solution with standard alkali failed to give concordant results owing to the difficulty of attaining a definite end point; it was noticed, however, that if the alkali was run in quickly, before phenylthiourea had time to separate from the aqueous solution, and the now turbid mixture was cleared by warming, the liquid, as it cooled, deposited first brilliant plates and then phenylthiourea in needles or prisms. When the solid was added directly to a slight excess (about 2 molecules) of *N*/10 alkali and the mixture warmed until it became clear, the solution, on cooling, deposited only the brilliant spangles; these were devoid of bitter taste and consisted of *ab*-acetylphenylthiocarbamide (m. p. 170—171°).

This transfer of the acetyl group to nitrogen seems to take place only with the ready formed hydrochloride, for when phenylthiourea was crystallised from solutions containing sodium acetate and chloride, or acetic and hydrochloric acids, or from the latter mixture after neutralisation by alkali, no sign could be detected of the production of *ab*-acetylphenylthiocarbamide. Moreover, when phenylthiourea, dissolved in weak caustic alkali (2 molecules), was treated with excess of acetyl chloride, the solution, on cooling, deposited nothing but unchanged phenylthiourea.

The symmetrical or *ab*-thiocarbamide, then, is formed on removal of the combined hydrogen chloride, whether this be effected by heat or by the action of caustic alkali in excess.

That a transfer of the acyl radicle from sulphur to nitrogen should take place under the influence of heat is not surprising, a number of cases having now been observed of the movement of an acid group from one nitrogen atom to another within the thiourea molecule. Thus, for instance, Wheeler has shown (*Amer. Chem. J.*, 1902, **27**, 270) that *aa*-acetylphenylthiocarbamide, $AcPhN{\cdot}CS{\cdot}NH_2$ (compare Hugershoff, *Ber.*, 1899, **32**, 3649), is changed by fusion into the *ab*-compound, $AcNH{\cdot}CS{\cdot}NHPh$, and Johnson and Jamieson (*ibid.*, 1906, **35**, 297), that various acyl-ψ-thioureas, for example, $Bz_2N{\cdot}C(SMe){:}NH$, undergo a like change, one acyl group moving from its original attachment in the amino-position and becoming united at the imino-group. In the case of our acylphenyl derivative, heat appears to determine that change whereby the most stable configuration is produced.

On the other hand, that the presence of dilute caustic alkali should lead under such mild conditions to the same ultimate result was both unexpected and puzzling. Water, as previously stated, removes the acetyl group from the hydrochloride, thereby producing phenylthiourea; and since phenylthiourea, in contact with alkali, resists acetylation by acetyl chloride, the final change, however accomplished, could scarcely be accounted for by initial hydrolysis of the additive compound into its original constituents. Presumably, therefore, the formation of *ab*-acetylphenylthiocarbamide must be explained either by some change occurring in the ψ-base itself, when liberated from its hydrochloride, or else through some influence exerted on the former by the alkali.

This could obviously be tested by removing the combined hydrochloric acid under conditions such as to preclude the resultant organic product from exposure to the action of free alkali, and noting if the product was still the same.

The first experiment in this direction was conducted by adding gradually to a solution of the hydrochloride (1 molecule) in nearly anhydrous alcohol, one equivalent of sodium previously dissolved in a separate portion of the same solvent, any material rise of temperature being prevented. The precipitate of sodium chloride was separated, and the clear, strongly acid filtrate allowed to evaporate spontaneously; this liquid gave no reaction for thiocyanic acid, thereby differing from solutions which had been treated with alkali to neutrality or in excess. On concentration, white crystals were deposited, free from chlorine, somewhat sparingly soluble in water, and containing both thiocarbamidic sulphur and the acetyl group. Our hope that dissociation of the original compound would be avoided by the use of strong (99 per cent.) alcohol instead of water was not realised, for the product melted very indistinctly at 129—132° and had a bitter taste, which proved to be due to its containing a very appreciable quantity of phenylthiourea. By means of cold chloroform, in which it is almost insoluble, the latter was separated; the chloroform was then evaporated, and the residue, when crystallised from dilute alcohol, obtained in long, pointed prisms, melting, if rapidly heated, at 139°. The alcoholic solution darkened gradually when mixed with neutral silver nitrate or at once on treatment with the ammoniacal nitrate; desulphurisation occurred readily on boiling with an alkaline solution of lead. The presence of an acetyl group was proved by warming the substance with alcohol and sulphuric acid, when the odour of ethyl acetate became distinct.

In the second experiment, the hydrochloride, dissolved as before in strong alcohol, was treated with pure, dry calcium carbonate; when the effervescence had ceased, the unattacked carbonate was removed by filtration, and on evaporating the filtrate to a small bulk at the atmospheric temperature, precisely the same results were obtained as when the hydrochloric acid was eliminated by means of sodium ethoxide, the purified end product resembling in every respect the substance melting at 139° previously described.

A sulphur determination gave the figures required for the free "base," $PhNH{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}CH_3$, or for its isomeride, *ab*-acetylphenylthiocarbamide, $PhNH{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}CH_3$:

0·194 absorbed 20·1 c.c. $N/10$ barium chloride. S = 16·6.

$C_9H_{10}ON_2S$ requires S = 16·50 per cent.

This substance, however, could not be *ab*-acetylphenylthiocarbamide, which crystallises in brilliant leaves melting at 170—171°, neither, on account of its comparatively high melting point, could it well be the "base" formulated above, since a compound having the structure of the latter might be expected to melt at about 50°. But as the phenyl group is undoubtedly attached to nitrogen, the only remaining isomeride proper to this series is a thiourea or thiocarbamide having both the phenyl group and the acetyl group attached to the same nitrogen atom, that is, assuming the compound to be a thiocarbamide, $AcPhN{\cdot}CS{\cdot}NH_2$.

That the substance in question had this composion was made certain by the following observations: (1) when heated at or slightly above its melting point it presently resolidified, being converted by the fusion into the isomeric *ab*-acetylphenylthiocarbamide; (2) when dissolved in weak aqueous caustic alkali it yielded the last-named symmetrical compound; (3) when treated with strong alkali the acidified mixture gave an intense reaction for thiocyanic acid. These are the properties of the substance obtained by Hugershoff (*loc. cit.*) by dissolving phenylthiourea in acetic anhydride at 80°; to this he incorrectly assigned the symmetrical or *ab*-formula, an error subsequently corrected by Wheeler (*loc. cit.*), who placed beyond doubt the fact of its being an *aa*-derivative. The chemical identity of our product with that of Hugershoff was further established by the observation that a specimen of his compound, prepared according to his directions, melted, within a degree, at the same temperature as ours, and when the two were mixed in equal proportions the melting point underwent no perceptible change.

These experiments show that caustic alkali determines by its presence a change in the product initially formed by the removal of the combined hydrochloric acid from our hydrochloride, since if this removal is effected with a limited quantity of alkali, or in the absence of any alkaline substance, the product is not identical, but isomeric with that obtained in presence of excess of alkali, and the former product, when isolated and then brought into contact with free alkali of a certain strength, is changed into the latter [see (2), above].

Summary of this Series of Changes.

(i) Phenylthiourea is not acetylated, in presence of alkali, by treatment with acetyl chloride, but

(ii) Acetyl chloride unites spontaneously with phenylthiourea to form the hydrochloride of a feeble "base," acetyl-ψ-v-phenylthiourea, $PhNH{\cdot}C(NH){\cdot}SAc$.

(iii) This base, when liberated in alcoholic solution, undergoes isomeric change, the acetyl group migrating, at the ordinary temperature, to the phenylated nitrogen atom to form $PhAcN{\cdot}CS{\cdot}NH_2$.

(iv) The last product, if heated or if brought into contact with dilute alkali, undergoes further isomeric change, the phenyl and acetyl groups now becoming attached to different nitrogen atoms, and thus yielding $AcNH{\cdot}CS{\cdot}NHPh$.

(v) The hydrochloride (ii) changes by melting, with loss of hydrogen chloride, into AcNH·CS·NHPh; by solution in cold water it yields phenylthiourea.

This succession of movements of the acetyl group is exhaustive; the acetyl, combined at first with sulphur, can be driven to the phenylamino-group, and thence, by an easy transition, to the remaining nitrogen atom; in other words, it may occupy in succession, and in a given existing phenylthiourea molecule, every place where, according to our present notions, it could conceivably be attached. No less than six distinct forms of acetylphenylthiourea may be formulated, namely, AcPhN·CS·NH_2, PhNH·CS·NHAc, NHPh·C(NAc)·SH, NHPh·C(NH)·SAc, NHAc·C(NH)·SPh, and AcPhN·C(NH)·SH; these are all essentially different, and do not include mere tautomeric variants (for example, PhNH·C(NH)·SAc $\rightleftarrows$ NH_2·C(NPh)·SAc), and there does not at present seem to be any valid reason for supposing that any one of them is incapable of existence. Nevertheless, in view of the free mobility of both hydrogen and acetyl in this very "plastic" molecule, it will doubtless be no easy matter to prepare and to keep the three forms which still remain unknown. Of these, one contains the aryl group combined with the sulphur atom; it may be noted in passing that all attempts hitherto made to fix the aryl group in this ψ-form have been unsuccessful (see Trans., 1906, **89**, 909).

In reference to Hugershoff's observation that *aa*-thiocarbamides containing one acyl and one aryl group yield thiocyanic acid on treatment with strong alkali,

$$\text{AcPhN·CS·NH}_2 + \text{KOH} = \text{AcNHPh} + \text{KSCN} + \text{H}_2\text{O},$$

a number of experiments were made in order to learn if this property is peculiar to members of that class. The compounds examined included (i) monosubstituted thioureas, both acyl and alkyl; (ii) disubstituted thiocarbamides, *aa*- and *ab*- of the alkyl or aryl series, or of mixed varieties, and *ab*-derivatives of the acyl-alkyl or acyl-aryl class; (iii) trisubstituted thioureas derived from acyl, aryl, and alkyl thiocarbimides by combination with secondary bases of various sorts. Without giving a detailed list of all the substances employed, it may suffice to say that not one of them afforded the slightest reaction for thiocyanic acid when treated with alkali followed by hydrochloric acid and ferric chloride. On the other hand, our acetyl-ψ-ν-phenylthiourea hydrochloride reacted readily for it, owing to partial conversion into Hugershoff's compound, and the same is true of the various additive compounds from acylogens and monosubstituted thioureas, which we describe in the following pages. This test, therefore, appears to be a characteristic one for compounds of the class named.

It is stated above that *aa*-acetylphenylthiocarbamide melted at 139°, the temperature recorded by Hugershoff (*loc. cit.*) for this compound. Nevertheless, we had at first much difficulty in reconciling the melting point of our product with that given by him, or indeed, in arriving at any really definite melting point. This was ultimately found to be due to the slowness with which we conducted the heating, for on working rapidly, the substance melted at 139°. At our own slow rate, not only did the substance melt at temperatures varying in different determinations from about 133° to 137°, but also, when a specimen of Hugershoff's compound (prepared from acetic anhydride according to his directions) was heated at the same time as ours, it showed a like behaviour. Moreover, the substance, if heated for some time at 129°, gradually softened, but did not liquefy, and on raising the temperature, no further change could be observed until between 150° and 160° or even a trifle higher, when it melted to a clear liquid.

It appeared doubtful, therefore, whether the compound really possessed a true melting point, for, since at a temperature many degrees below that of liquefaction, considerable change may occur within not many minutes (into the *ab*-compound), it was to be expected that at about 139° this change would be very rapid. Such, in fact, is the case, for if the compound, heated quickly, was removed the instant it liquefied and cooled at once, the now solid material, when put back into the apparatus, even at 145°, no longer melted, thus showing that the process of conversion had gone far. The solidified product also, when tested with alkali, gave but a trifling reaction for thiocyanic acid.

Now although the rate of change is very rapid indeed at the liquefying point, it is considerably retarded at temperatures not far removed from this, and hence it seemed probable that the liquefaction was conditioned, not by the melting of the *aa*-compound, with subsequent change to the *ab*-form, but through the production of a mixture of both in proportions continuously varying, so that at some particular moment the most fusible mixture would result; in which case, if the temperature was high enough, it must melt.

The following experiment seems to confirm this view. Two narrow tubes, as nearly equal in all respects as possible, were charged to the same depth with two fine powders, one consisting of the *aa*-compound, the other of a substance melting at 141—142°. The bath being kept steadily at 143°, both tubes were immersed simultaneously and attached to the same thermometer. In ten seconds, the substance of higher melting point liquefied suddenly; after a total interval of forty-five seconds, the *aa*-compound, which meanwhile had scarcely changed in appearance, also suddenly melted. Ten seconds, therefore, were required for the establishment inside the tubes of a temperature not less than 141—142°, which is above the maximum "melting point" of the *aa*-derivative; presumably the remaining thirty-five seconds were occupied, not in melting it, but in effecting such a relative amount of conversion as to produce a mixture fusible at the temperature already attained within the tube.

Acetyl Chloride and o-*Tolylthiourea.*

When to a saturated solution of *o*-tolylthiourea in cold acetone rather more than the calculated quantity of acetyl chloride was added, and the mixture cooled, a crystalline, white solid was soon deposited, melting at 96° with effervescence; the same product was obtained, with evolution of heat, by mixing the constituents in presence of benzene, the latter method giving 95 per cent. of the theoretical yield for a molecular additive compound:

0·2445 required 9·8 c.c. $N/10$ silver nitrate. $Cl = 14·2$.

$C_{10}H_{12}ON_2S,HCl$ requires $Cl = 14·50$ per cent.

The pure substance dissolved readily in cold water, yielding an acid solution, from which in a short time white crystals of *o*-tolylthiourea began to separate; in the solution both hydrochloric and acetic acids were present, but no thiocyanic acid.

When heated slightly beyond its melting point it effervesced freely, evolving fumes of hydrogen chloride; the liquid now resolidified, and the solid, when recrystallised from boiling alcohol, in which it was rather sparingly soluble, formed brilliant prisms. The cold alcoholic solution gave immediately, with aqueous silver nitrate, a black precipitate, and had an odour of ethyl acetate when warmed with sulphuric acid. The melting point of this new product, 182—183°, was less than a degree below that of a specimen of pure *ab*-acetyl-*o*-tolylthiocarbamide, and when equal weights of the two were mixed, the melting point of the mixture was still 182—183°.

In this case, therefore, as in that of the phenylic homologue, withdrawal of the combined hydrochloric acid by heat is associated with movement of the acetyl group from sulphur to nitrogen, acetyl-*ψ*-*o*-tolylthiourea hydrochloride changing to *ab*-acetyl-*o*-tolylthiocarbamide,

$$NHPh{\cdot}C(NH){\cdot}SAc,HCl = HCl + NHPh{\cdot}CS{\cdot}NHAc.$$

The solution of the hydrochloride, if mixed without delay with aqueous picric acid, gave a yellow *picrate* in minute needles.

By treating the hydrochloride, dissolved in absolute alcohol, with one equivalent of sodium ethoxide, separating the precipitated sodium chloride, and treating the crystalline residue left by evaporation of the alcohol, as described in the corresponding experiment with the phenyl derivative, white prisms were obtained melting at 139·5°. They were free from chlorine, gave the usual desulphurisation reactions with lead and silver salts, and when treated with strong alkali yielded a pasty mass, reacting abundantly for thiocyanic acid. This product was obviously Hugershoff's *aa*-acetyl-*o*-tolylthiocarbamide, melting point 140°:

0·208 gave 0·2318 $BaSO_4$. S = 15·3.

$C_9H_{10}ON_2S$ requires S = 15·38 per cent.

It may here be noted that the hydrochloride, both on heating and on treatment with sodium ethoxide, had an odour of thioacetic acid, owing probably to partial decomposition of the "base" when liberated:

$$C_7H_7\cdot NH\cdot C(NH)\cdot S\cdot COMe = C_7H_7\cdot N{:}C{:}NH + COMe\cdot SH.$$

Acetyl Chloride and p-*Tolylthiourea.*

p-Tolylthiourea is so sparingly soluble in acetone that the precipitation method is not well suited for preparing the additive compound except on a small scale; when obtained in this way it formed lanceolate prisms. It was prepared in larger quantity by mixing together the finely-powdered thiourea and acetyl chloride, whereupon sufficient heat was evolved to evaporate a portion of the latter; the mixture was then ground up in a mortar, the solid collected at the pump, washed with light petroleum, and dried in a vacuum. The melting point was 102—103° with much effervescence, and the yield amounted to 80 per cent. of the theoretical:

0·2445 required 9·8 c.c. *N*/10 silver nitrate. Cl = 14·2.

$C_{10}H_{12}ON_2S,HCl$ requires Cl = 14·50 per cent.

If not contaminated with unchanged *p*-tolylthiourea (which may be extracted by repeatedly shaking the powder with acetone) the hydrochloride dissolved readily in water, the solution quickly becoming turbid from the separation of *p*-tolylthiourea; no thiocyanic acid was contained in the liquor. The thiourea melted at 181°; Staats (*Ber.*, 1880, **13**, 136) gives 182°.

When the hydrochloride was treated with cold aqueous caustic alkali the mixture reacted readily for thiocyanic acid, thereby showing the formation of the *aa*-acetyl-*p*-tolylthiocarbamide.

Acetyl Chloride and ab-*Diphenylthiocarbamide.*

According to Deninger (*Ber.*, 1895, **28**, 1322), thiocarbanilide cannot be acetylated by the Schotten-Baumann method; similarly, we found (see p. 131) that phenylthiourea is not acetylated by acetyl chloride in presence of caustic alkali.

When, however, diphenylthiocarbamide, suspended in benzene, was mixed with excess of acetyl chloride, the solid gradually changed to a clear, yellow oil, which crystallised on standing. The product, when powdered and washed thoroughly with benzene, was a white powder, fuming in moist air, and having an odour of hydrochloric acid; it was apparently insoluble in water, and began to decompose, with effervescence, at about 106°:

0·3065 absorbed 9·7 c.c. *N*/10 silver nitrate. C = 11·24.

$C_{15}H_{15}ON_2ClS$ requires Cl = 11·58 per cent.

The yield amounted to only 50 per cent. of that calculated for a molecular additive compound. Dilute alkali withdrew all the combined acid, leaving thiocarbanilide.

The compound of diphenylthiocarbamide with acetyl chloride is distinctly less stable than that of monophenylthiourea, since the former evolves visible fumes when exposed to moist air, whilst the latter does not.

Acetyl Chloride and di-o-*Tolylthiocarbamide.*

On mixing these together, using excess of acetyl chloride, a yellow liquid was formed; this, when treated with light petroleum, gave a paste which presently solidified. The product, when broken up and dried, had little odour, and melted sharply, with copious effervescence, at 135—136°:

0·3345 required 9·7 c.c. *N*/10 silver nitrate. Cl = 10·3.

0·3345 gave 0·262 $BaSO_4$. S = 10·8.

$C_{17}H_{19}ON_2ClS$ requires Cl = 10·6; S = 10·45 per cent.

Benzoyl Chloride and Thiourea.

These substances combined at once in presence of benzene to form a white powder melting at about 116°; the yield was poor, amounting to only 54 per cent. of the theoretical:

0·2165 required 9·7 c.c. *N*/10 silver nitrate. Cl = 15·9.

$C_8H_8ON_2S,HCl$ requires Cl = 16·4 per cent.

When the combined acid was removed by adding calcium carbonate to a solution of the hydrochloride in 99 per cent. alcohol, no benzoylthiourea was found in the filtrate, but ordinary thiourea instead; this behaviour is similar to that observed in the case of the corresponding acetyl compound (see p. 126) when treated with a limited amount of sodium ethoxide.

Reference has already been made to Pike's observation that thiourea and benzoyl chloride if heated to 120° yield benzoylthiourea; an attempt was therefore made to ascertain whether the latter substance would be produced by heating the above additive compound.

A quantity was melted in a test-tube, immersed in a sulphuric acid bath: hydrogen chloride and a little hydrogen sulphide were evolved, and soon the mass solidified; the temperature was now raised to 125° to complete the action, and after some five minutes the tube was removed and cooled. The product, nearly insoluble in cold water, was boiled with a large quantity of this solvent and the solution filtered from a trace of pasty solid. The filtrate crystallised immediately, giving small, vitreous prisms which dissolved readily in cold alkali; this solution, when mixed with a lead salt and heated, was desulphurised with formation of a speculum of lead sulphide. The solid had an intensely bitter taste; it was easily soluble in hot alcohol, somewhat sparingly so in cold, and the solution, when warmed with sulphuric acid, had an odour of ethyl benzoate. It crystallised from boiling water in needles melting at 169—170°, and hence consisted of benzoylthiourea, which melts according to Pike (*loc. cit.*) at 169—170°.

There can be no doubt as to the position of the acyl group in benzoylthiourea, since Miquel has shown (*Ann. Chim. Phys.*, 1877, [v], 11, 313) that it is produced from benzoylthiocarbimide and ammonia. By heating the additive compound, therefore, it loses hydrogen chloride, and the benzoyl group thereupon transfers itself from the sulphur to one of the nitrogen atoms.

Benzoyl chloride gave with phenylthiourea a tenacious paste; with *o*-tolylthiourea it yielded a solid additive product which was not examined in detail.

Benzoyl Chloride and p-*Tolylthiourea.*

By direct union of these constituents a soft, white powder, decomposing with effervescence at 137—138°, was obtained in nearly quantitative yield. The substance melted in boiling water, and the filtrate, on cooling, deposited long needles, which were, apparently, benzoic acid. It was desulphurised by alkaline solution of lead, and when warmed with alcohol and sulphuric acid gave the odour of ethyl benzoate:

0·613 required 20·1 c.c. *N*/10 silver nitrate. Cl = 11·6.

$C_{15}H_{14}ON_2S,HCl$ requires Cl = 11·5 per cent.

On warming the substance with caustic alkali and treating the resulting mixture with hydrochloric acid, followed by ferric chloride, a blood-red coloration appeared; as this reaction points in the case of acetyl derivatives of monosubstituted thioureas to the presence of an *aa*-disubstitution compound, it seemed probable that the thiocyanic acid yielded by the benzoyl derivative had a like origin. Hugershoff does not appear to have inquired whether the benzoyl radicle is similar to the acetyl group as regards the power of forming labile thiocarbamides; we therefore conducted the following experiment to learn whether, from our supposed benzoyl-*ψ*-*p*-tolylthiourea hydrochloride, $C_7H_7\cdot NH\cdot C(NH)\cdot S\cdot COPh,HCl$, an *aa*-derivative could be produced, $PhCO\cdot N(C_7H_7)\cdot CS\cdot NH_2$ [or perhaps $PhCO\cdot N(C_7H_7)\cdot C(NH)\cdot SH$], convertible in turn into the known *ab*-benzoyl-*p*-tolylthiocarbamide, $PhCO\cdot NH\cdot CS\cdot NH\cdot C_7H_7$.

From a quantity of the freshly-prepared hydrochloride, dissolved in cold anhydrous alcohol, the combined acid was withdrawn by excess of calcium carbonate, the filtered liquor was then evaporated, and the solid residue purified by chloroform in the manner previously described for the corresponding acetylphenyl derivative. The viscid solid, left by evaporation of the chloroform, was treated with pure ether, which separated it into (1) a residue, giving no thiocyanic reaction with alkali, and melting after one recrystallisation from alcohol at 157—158°, and after a second at 158—159° (uncorr.), and (2) a filtrate. The latter on evaporation left a solid, reacting with alkali for thiocyanic acid. On crystallising this from alcohol, needles melting at 157—158° were obtained, resembling the preceding and giving no thiocyanic reaction; moreover, the liquor from these now reacted but faintly with alkali for thiocyanic acid.

The substance melting at 158—159° proved to be a thiocarbamide containing the benzoyl group, and since it gave no thiocyanic acid, was presumably not the *aa*- but the *ab*-compound, namely, benzoyl-*p*-tolylthiocarbamide. This melting point is materially lower than that recorded by Miquel (*loc. cit.*), namely, 165°. On preparing Miquel's compound, however, by his own method (from benzoylthiocarbimide and *p*-toluidine), and recrystallising from alcohol until the melting point became constant, a substance was obtained identical in appearance and properties with that described above, and melting sharply at the same temperature, 158—159° (uncorr.). Miquel's figure, therefore, is somewhat too high.

So far as may be judged from the single set of experiments detailed above, it would seem that the hydrochloride of benzoyl-*ψ*-*p*-tolylthiourea can yield, by the elimination of its combined hydrochloric acid, *aa*-benzoyl-*p*-tolylthiocarbamide, but that the latter, being rather unstable, is resolved by successive recrystallisations from hot alcohol into the stable or *ab*-isomeride, $PhCO\cdot NH\cdot CS\cdot NH\cdot C_7H_7$.

Benzoyl Chloride and Thiocarbanilide.

When brought together in presence of benzene these substances did not appear to unite, but on mixing them together directly there was vigorous combination, with considerable evolution of heat. After being washed with benzene, followed by light petroleum, the product was slightly yellow, and decomposed at 108—109°. Yield, 90 per cent. of the theoretical. This substance was distinctly unstable, the loss of material being perceptible during the process of weighing out for analysis

0·3784 required 9·5 c.c. *N*/10 silver nitrate. Cl = 8·9.

$C_{20}H_{17}ON_2ClS$ requires Cl = 9·6 per cent.

In addition to the experiments described above, the following substances were examined as to their power of combination when mixed together:

Acetyl chloride and *ab*-acetylphenylthiocarbamide.

Acetyl chloride and *ab*-benzoyl-*o*-tolylthiocarbamide.

Ethyl chlorocarbonate and *ab*-benzoyl-*o*-tolylthiocarbamide.

Acetyl chloride and carboxy-*o*-tolylthiourea,

$C_7H_7\cdot CO_2\cdot NH\cdot C(NH)\cdot SH.$

Ethyl chlorocarbonate and carboxy-*o*-tolylthiourea,

$C_7H_7\cdot CO_2\cdot NH\cdot C(NH)\cdot SH.$

o-Tolylchlorocarbonate and carboxy-*o*-tolylthiourea,

$C_7H_7\cdot CO_2\cdot NH\cdot C(NH)\cdot SH.$

No action seemed to occur; in each case the thiocarbamide employed was recovered and its melting point verified. The presence of an electronegative group in a thiourea appears, therefore, to paralyse, or at least greatly to hinder, its power of combining with acylogens.

In all the preceding cases of combination the radicle R·CO· of the acid chloride employed was highly electronegative in character. With the chloride R·O·COCl, the radicle of which is much more electropositive, the products as a rule were comparatively stable. Thus, ethyl and methyl chlorocarbonates, when united with thiourea, gave compounds which did not appear to be dissociated by cold water to any material extent, whilst the compounds of methyl chlorocarbonate with phenyl-, *o*-tolyl-, and *p*-tolyl-thiourea respectively, were not dissociated at all; in fact, when treated with caustic alkali, their solutions yielded the corresponding bases, for example,

PhNH·C(NH)·S·CO·OMe

(Dixon, Trans., 1903, **83**, 550). The hydrochloride obtained from thiourea and phenyl chlorocarbonate (Dixon, Trans., 1906, **89**, 909) is a well-marked salt; the base, however, could not be isolated by means of alkali, probably because of the feebly positive character of the radicle PhO·CO.

Now, if it be true that the general stability of these combinations, and in particular their power of resisting the hydrolysing action of water, depends mainly on the nature of the acyl radicle united with the sulphur atom; it should be possible, by employing acylogens containing groups less strongly negative than acetyl and its congeners, to obtain hydrochlorides proportionately more stable in the sense named than the above. We have tested this conjecture experimentally, and so far as may be judged from the following results it appears on the whole to be substantiated.

Of acylogens suitable for the purpose, no abundant choice was available; we selected for investigation the chlorides of certain substituted carbamic acids, $R_2N\cdot CO\cdot OH$, since the group $R_2N\cdot CO\cdot$ is distinctly less negative than the acetyl group.

Diphenylcarbamic Chloride and Thiourea.

Molecular proportions were thoroughly mixed and heated in an oil-bath until liquefaction commenced and a trace of effervescence set in; at this stage the temperature of the bath was 134°. When cool, the solid residue was powdered, boiled with acetone (which dissolves it to a very appreciable extent), filtered, and washed with more cold acetone; the yield of nearly white powder reached only 55 per cent. of the amount calculated from the equation

$$Ph_2N\cdot COCl + NH_2\cdot C(NH)\cdot SH = NH_2\cdot C(NH)\cdot S\cdot CO\cdot NPh_2,HCl,$$

but a further considerable quantity separated from the acetone solution.

The hydrochloride was moderately easily soluble in warm water; it crystallised from this solvent in short, vitreous prisms having a somewhat greasy lustre and melting, with copious effervescence, at 182—183° (uncorr.):

0·3075 required 9·9 c.c. *N*/10 silver nitrate; Cl = 11·4.

$C_{14}H_{14}ON_3ClS$ requires Cl = 11·54 per cent.

Water, therefore, did not destroy the salt.

The aqueous solution was neutral to litmus; when treated in the cold with rather less than one equivalent of normal alkali, it gave a crystalline white precipitate, which consisted, not of the expected free base, but of diphenylamine; cold alkaline solution of lead gave with the liquor a black precipitate, thus showing that the disruption of the molecule had gone far.

When treated with dilute nitric acid or with a solution of potassium nitrate, the aqueous solution of the hydrochloride yielded a crystalline, white precipitate; the latter, by recrystallisation from boiling water, was obtained in clear, colourless, flattened, oblique prisms free from chlorine, darkening at 170°, and frothing at 176—177°. That this substance was a *nitrate* was shown both by the ferrous sulphate test and by the fact that on warming it with dilute alkali and then treating the mixture with sulphuric acid, a splendid indigo-blue coloration appeared; this is explained by the liberation by the alkali of diphenylamine, which in presence of a nitrate and sulphuric acid gives the well-known blue diphenylamine reaction:

0·334 required 20·5 c.c. *N*/10 barium chloride; S = 9·8.

$C_{14}H_{13}ON_3S,HNO_3$ requires S = 9·58 per cent.

Aqueous picric acid, when mixed with a cold saturated solution of the nitrate, gave the corresponding *picrate* in minute, yellow needles rather sparingly soluble in boiling water.

Phenylmethylcarbamic Chloride and Thiourea.

Combination occurred on the water-bath, and after treatment with acetone, as described in the preceding case, the yield of white solid reached 63 per cent. of the theoretical; the product melted with effervescence at about 175°, and when dissolved in water gave a neutral solution. Chlorine was determined by acidifying the aqueous solution with nitric acid, filtering, and treating the filtrate according to Volhardt's method:

0·2445 required 9·65 c.c. $N/10$ silver nitrate; Cl = 14·0.

$C_9H_{12}ON_3ClS$ requires Cl = 14·47 per cent.

On adding dilute nitric acid (or potassium nitrate) to the aqueous solution the *nitrate* was precipitated, which crystallised from boiling water in white, lustrous needles, becoming yellow at 155°, and melting with effervescence to a black liquid at 162°. The solution was desulphurised by boiling with ammoniacal silver nitrate, and gave the usual reactions for nitric acid:

0·272 required 20·45 c.c. $N/10$ barium chloride; S = 12·0.

$C_9H_{11}ON_3S,HNO_3$ requires S = 11·76 per cent.

The *picrate* crystallised from water in small, yellow needles melting with effervescence at 174—175°.

Phenylethylcarbamic Chloride and Thiourea.

Prepared by warming the constituents on the water-bath and treating as previously described; the nearly white product melted at 160° with effervescence:

0·2595 absorbed 9·9 c.c. $N/10$ silver nitrate; Cl = 13·9.
0·2595 „ 9·9 c.c. $N/10$ „ Cl = 13·9.
0·2595 „ 19·8 c.c. $N/10$ barium chloride; S = 12·2.

$C_{10}H_{14}ON_3ClS$ requires Cl = 14·07; S = 12·33 per cent.

The nitrate, precipitated as before, crystallised from boiling water in vitreous prisms changing in appearance at 145°, and melting with frothing and green coloration at 154°:

0·2595 required 18·7 c.c. $N/10$ barium chloride; S = 11·5.

$C_{10}H_{13}ON_3S,HNO_3$ requires S = 11·18 per cent.

A crystalline *picrate* melting at 160° was obtained from the mother liquor of the nitrate; phenylethylcarbamylthiourea (from the corresponding thiocarbimide and ammonia) when treated in alcoholic solution with picric acid gives no picrate.

Phenylbenzylcarbamic Chloride and Thiourea.

The hydrochloride, being somewhat impure, was dissolved in water and precipitated as *nitrate*, which crystallised from boiling water in long, stout needles changing colour at 145° and effervescing at 154°:

0·348 gave 0·235 $BaSO_4$; S = 9·3.

$C_{15}H_{15}ON_3S,HNO_3$ requires S = 9·19 per cent.

A crystalline *picrate* was obtained melting at 161°; on analysis:

0·2185 gave 30·8 c.c. moist nitrogen at 17° and 773 mm. N = 16·64.

$C_{21}H_{18}O_8N_6S$ requires N = 16·34 per cent.

Benzyl Chlorocarbonate and Phenylthiourea.

Reference has already been made in an earlier part of this paper (p. 123) to the fact that alkyl chlorocarbonate derivatives of certain thioureas, when treated with alkali, do not behave in the same way as the corresponding compounds obtained from aryl chlorocarbonates. In so far as benzyl chlorocarbonate, although containing an aromatic group, is allied rather to the former class, it seemed probable that its compound with phenylthiourea would tend to pass readily into benzyl-ψ-phenylthiourea, $NHPh{\cdot}C(NH){\cdot}S{\cdot}C_7H_7$, and an experiment was made in order to learn if this would be the case. As no special interest attached to the production of the additive compound of the two substances named above, the preparation was made under the influence of heat, which it was expected would decompose the additive compound as fast as formed, with elimination of carbon dioxide, but not of hydrogen chloride; in effect, this proved to be the case.

When phenylthiourea was heated on the water-bath with a slight excess of benzylchlorocarbonate in presence of benzene, carbon dioxide escaped with effervescence, and an oil was formed, which presently solidified; the solid, after being washed, first with benzene and then with light petroleum, amounted to 97 per cent. of the yield calculated from the equation

$$CSN_2H_3Ph + PhCH_2{\cdot}COCl = CO_2 + PhNH{\cdot}C(NH){\cdot}S{\cdot}CH_2Ph,HCl.$$

3·52 grams of the product, dissolved in 500 c.c. of water, were treated with excess of normal alkali, the solid precipitate was then separated, and the filtrate neutralised with normal sulphuric acid, using phenolphthalein as indicator; 10·5 c.c. of alkali were absorbed by the combined hydrochloric acid, instead of 10·9, as required by the above formula.

The residual white powder, having an odour of benzyl mercaptan, crystallised from light petroleum in brilliant, pearly leaves, melting at 80°, which were insoluble in water, easily soluble in alcohol or in hydrochloric acid; this solution gave a crystalline *picrate* and a white *mercurichloride.* The alcoholic solution was not affected by silver nitrate, but the mixture, when treated with ammonia and warmed, gave a yellow, flocculent precipitate, and the solution in alcoholic potash, when heated with a lead salt, was not blackened, but yielded instead a bright yellow precipitate. The substance was obviously Werner's ψ-base, obtained by him from phenylthiourea and benzyl chloride (Trans., 1890, **57**, 295); for this he gives the melting point 81—82°, whilst our compound, once recrystallised, melted at 80°.

With thiourea and benzyl chlorocarbonate similar results were obtained, and eventually Werner's thiourea base,

$$NH_2\cdot C(NH)\cdot S\cdot CH_2Ph,$$

(*loc. cit.*) was isolated.

Summary and Conclusion.

In the following summary of the principal observations described or referred to above, the statements have occasionally been put in somewhat general terms, although the number of cases tested may have been few.

(i) Acetyl chloride or benzoyl chloride combines in molecular proportion with thiourea to form the hydrochloride of a "base" or ψ-thiourea, in which the acyl group is joined to the rest of the molecule through the sulphur atom, as shown by the typical formula $NH_2\cdot C(NH)\cdot S\cdot CO\cdot CH_3$.

By treatment of the hydrochloride with water, or by treatment of its alcoholic solution with one equivalent of sodium ethoxide, or with excess of calcium carbonate, thiourea is regenerated; if, however, the compound is melted, it loses hydrogen chloride only, the acyl group migrating to the nitrogen atom so as to produce acetyl- or benzoyl-thiourea. The hydrochloric acid may be displaced by picric acid, with formation of a sparingly soluble picrate of the base.

(ii) Acetyl chloride or benzoyl chloride unites similarly with aryl monosubstituted thioureas, the products being quickly dissociated by water, as in the preceding cases; it is possible, nevertheless, to obtain a picrate from the hydrochloride. On treating the hydrochloride in alcoholic solution with excess of calcium carbonate or with one equivalent of sodium ethoxide, the combined hydrogen chloride is eliminated, but (although the odour of thioacetic acid becomes perceptible) not with formation of the corresponding ψ-base, for example, $ArNH\cdot C\cdot(NH)\cdot S\cdot COCH_3$; instead, the acyl radicle migrates to the nitrogen atom combined the aryl group, thus producing the isomeric *aa*-disubstituted thiocarbamide, for example, $PhAcN\cdot CS\cdot NH_2$. Under the action of heat or of dilute alkali, or, it may be, even by recrystallisation, the latter again changes, owing to further acyl migration, into an *ab*-disubstituted thiocarbamide. When melted, the above additive compounds lose hydrogen chloride, thereby changing directly into *ab*-disubstituted thiocarbamides, AcNH·CS·NHAr.

(iii) Acetyl chloride or benzoyl chloride unites additively with aryl-disubstituted thiocarbamides; the products have not yet been examined in sufficient detail to justify a definite statement as to how the acyl radicle is attached.

(iv) Disubstituted carbamic chlorides unite with thiourea, forming haloid salts of basic forms, $XYN\cdot CO\cdot S\cdot C(NH)\cdot NH_2$; the nitrates and picrates of such bases are sparingly soluble in water. Caustic alkali destroys the hydrochlorides without liberating a corresponding base, the group XYN·CO· undergoing ready hydrolysis into secondary amine and carbon dioxide.

(v) If benzyl chlorocarbonate, $PhCH_2\cdot O\cdot COCl$, is warmed with thiourea or with phenylthiourea, carbon dioxide escapes, and a compound is formed such as $NH_2\cdot C(NH)\cdot S\cdot CH_2Ph$, in which the benzyl group is attached to the sulphur atom. Aliphatic chlorocarbonates behave similarly.

(vi) Organic acyl chlorides do not appear to be capable of uniting with a thiourea or thiocarbamide containing a distinctly acid radicle. The organic group of such a chloride, however, sometimes expels from an acid-substituted thiocarbamide, and replaces, a radicle more highly electronegative than itself.

Chemical Department,
Queen's College, Cork.

XIV.—*Transformations of Highly Substituted Nitroaminobenzenes. II. s-Tribromo-1-nitroaminobenzene.*

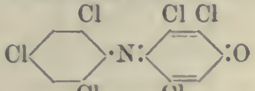
By Alice Emily Smith and Kennedy Joseph Previté Orton.

In earlier papers (Trans., 1902, 81, 806; 1905, 87, 389) we described certain reactions which are exhibited by *s*-trichloro-1-nitroaminobenzene when treated with sulphuric acid in acetic acid solution. It was shown that within certain limits of temperature and concentration of the sulphuric acid, the nitroamine yielded some 30—35 per cent. of a *s*-trichlorophenyliminotrichlorobenzoquinone (hexachloroquinoneanil). It was found possible, in bringing about this change, to avoid any displacement of chlorine by the nitro-group, and consequent formation of a dichloronitroaniline. In the case of the corresponding *s*-tribromo-1-nitroaminobenzene, on the other hand, it was observed that there was a far greater tendency for the bromine atom to leave the benzene nucleus, and in preliminary experiments such treatment as that described led mainly to the production of 2 : 6-dibromo-4-nitroaniline.

A number of experiments have, however, led to the discovery that *s*-tribromonitroaminobenzene will under narrowly-defined conditions yield phenyliminobenzoquinones analogous to those obtained from *s*-trichloronitroaminobenzene. This change is effected by solutions of sulphuric acid in acetic acid containing a certain small percentage of water. The concentration of sulphuric acid, which has been found most suitable, is 0·6 of sulphuric acid to 1 of acetic acid; with such a solution the reaction is brought to completion in one to two hours; higher concentrations of acid hasten the decomposition, but then the dibromonitroaniline is the main product. At lower concentrations the decomposition is so slow that secondary reactions greatly decrease the yield of the quinoneanil. Using the most favourable concentrations of sulphuric acid, it is only possible to obtain the quinoneanils if the temperature is kept as low as possible, that is, at the freezing point of the solution; at higher temperatures, the formation of nitroaniline again predominates. Addition of small quantities of water to the reacting mixture decreases the rate of the decomposition, but, at the same time, there is a falling off in the formation of the nitroaniline. About 4 per cent. of water is the most favourable concentration for the formation of the quinoneanil.

Although it is possible to prevent the formation of the dibromonitroaniline, the elimination of a certain proportion of bromine could not be avoided. As a result, a mixture of quinoneanils is obtained, in which the *s*-tribromophenyliminodibromobenzoquinone largely predominates over the *s*-tribromophenyliminotribromobenzoquinone.

This elimination of bromine and consequent formation of pentabromoquinoneanil is of considerable interest and throws some light on the mechanism of the formation of the quinoneanil from the nitroamine. The conversion of *s*-trichloronitroaminobenzene into a *s*-trichlorophenyliminotrichlorobenzoquinone,



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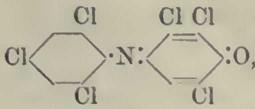
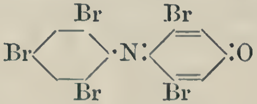


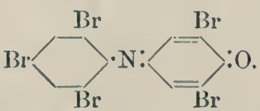
necessitates the transference of a chlorine atom from one carbon atom to the neighbouring carbon atom in the benzene ring. The like holds for the formation of a hexabromoquinoneanil from the tribromonitroaminobenzene. But in the transformation of the bromo-compound, although the bromine is set free from its original point of attachment, only a certain proportion, and that the smaller, re-enters the benzene nucleus. In the case of the trichloronitroamine, a complete re-entrance of the chlorine may take place; nevertheless, since at higher temperatures the presence of chlorine in small quantity can be detected among the products of the reaction, the difference between the tribromo- and trichloro-nitroamines is rather one of degree.

The other characters of the decomposition of the tribromonitroaminobenzene generally resemble those of the trichloro-compound (*loc. cit.*); the quinoneanil represents some 30—35 per cent. of the nitroamine, and an equivalent amount of ammonia is produced. The remainder of the nitroamine is represented by *s*-tribromobenzenediazonium salts. The proportion of penta- and hexa-bromoquinoneanil appears to vary considerably in different experiments, but the latter never exceeds a small percentage of the solid product of the reaction.

The constitution of the pentabromoquinoneanil partly follows from the cleavage with sulphuric acid, when it yields *s*-tribromoaniline and 2:6-dibromobenzoquinone. It is accordingly represented by one of the formulæ:



or



The halogen derivatives of 4-hydroxydiphenylamine are, with the exception of a tetrachlorohydroxydiphenylamine (prepared indirectly by Jacobson, *Chem. Centr.*, 1898, ii, 36), unknown. Notwithstanding that hydroxydiphenylamine itself is prepared very easily by Calm's method from aniline and quinol, there is no record of attempts at chlorination and bromination. We hoped to obtain the bromohydroxydiphenylamines, which are produced from the nitroamine, by direct bromination; to that end many experiments have been made, but it has been found that the bromination is no simple matter; such results as have been achieved will be shortly recorded.

The study of the transformations of the nitroamines is being continued.

EXPERIMENTAL.

Decomposition of s-*Tribromonitroaminobenzene.*

The products of the decomposition of *s*-tribromonitroaminobenzene (which was prepared by the method previously recorded, Trans., 1902, 81, 808) in acetic acid solution by sulphuric acid are very dependent on the conditions, namely, temperature, and the amounts of water and sulphuric acid present.

Generally speaking, the higher the temperature, and the larger the amount of sulphuric acid, the larger is the proportion of 2 : 6-dibromonitroaniline produced, and consequently of bromine eliminated. When the proportion (by weight) of the sulphuric acid to the acetic acid is above 1 : 1, the aniline is the main product; with lower proportions of sulphuric acid, but at slightly elevated temperatures, 20° to 30°, a similar result follows.

The 2 : 6-*dibromo-4-nitroaniline* was obtained in characteristic yellow crystals melting at 203°, and sparingly soluble in alcohol.

0·1654 gave 0·2092 AgBr. Br = 53·85.

$C_6H_4O_2N_2Br_2$ requires Br = 54·04 per cent.

As the proportion of sulphuric acid is decreased to 0·6 : 1, and rising of the temperature above freezing point of the solution prevented, the rate of the decomposition becomes slower; at the same time the yield of the nitroaniline decreases, and, with the concentration of the sulphuric acid just mentioned, is very small, a red substance (a mixture of bromoquinoneanils) being now the main solid product. Further lowering of the proportion of sulphuric acid is followed by such a decrease in the speed of the decomposition, that the nitroamine only disappears entirely after many hours' standing.

The effect of addition of water to the mixture is mainly to decrease the rate of the decomposition, but at the same time with a given concentration of sulphuric acid the production of dibromonitroaniline is less. A mixture of 30 grams of acetic acid and 18 grams of sulphuric acid, in which 1 gram of nitroamine was dissolved, contained no nitroamine after forty minutes, when so much water was present as to produce a 2 per cent. solution. If, however, the concentration of the water was 4 per cent., the time required for complete decomposition was one hour and twenty minutes. In the latter case, only a trace of dibromonitroaniline was formed, whilst in the solution containing 2 per cent. of water some 5 per cent. of the nitroamine is converted into the nitroaniline.

Preparation of the Red Solid (*Mixture of Bromoquinoneanils*).—In order to prepare the mixture of bromoquinoneanils as free from dibromonitroaniline as possible, the following procedure was finally adopted.

A solution of 50 c.c. of concentrated sulphuric acid (95 per cent.) in 50 c.c. acetic acid was slowly added to a solution of 5 grams of the nitroamine in 100 c.c. of acetic acid, the liquid being well stirred and cooled until a slight separation of the solid solvent occurred. The first addition of the sulphuric acid led to the development of a bluish-green colour, which finally changed to a deep olive-green. The liberation of bromine during the addition was very obvious. The mixture was allowed to stand, generally for about one hour, and then poured on to ice, when a red solid separated; this was collected and washed free from acid with water. Any unchanged nitroamine was removed by digestion with cold aqueous sodium carbonate; the red solid was then dried over sulphuric acid in an evacuated desiccator.

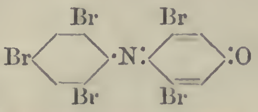
Examination of the Filtrate from the Red Solid.—The acid filtrate was of a yellow colour and had a strong odour of bromine. The estimation of the amount of bromine showed that some 26 per cent. of one atomic preparation of the bromine in the nitroamine had been eliminated.

The presence of *s*-tribromobenzenediazonium salt in the filtrate could be demonstrated by coupling, but was most clearly shown by conversion of the diazo-compound into *s*-tribromobenzene. To this end, an aliquot part of the filtrate was heated with one-third of its volume of alcohol. On cooling, *s*-tribromobenzene crystallised in long needles melting at 119—120°.

Separation of the Bromoquinoneanils.—Although it is not difficult to obtain the pure pentabromoquinoneanil, albeit with considerable loss, from the red solid, the separation of both the penta- and hexa-bromoquinoneanils is a matter of great difficulty. Repeated crystallisation from alcohol, acetic acid, or light petroleum, finally yielded a small quantity of the pentabromo-derivative of the correct melting point, 171°. The mother liquors deposited a substance, melting indefinitely between 135° and 150°, which could not be further dealt with by simple crystallisation.

The following method of treating the red solid has proved the most successful. The solid was extracted four or five times with small quantities of boiling light petroleum (b. p. 95°). The melting point of the undissolved residue gradually rose from 135—140°, the original melting point, to 160°. This residue was then dissolved in a mixture of equal volumes of benzene and petroleum, from which solution the pentabromoquinoneanil separated in the pure state, melting at 171°.

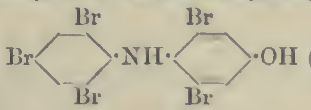
2 : 4 : 6-*Tribromophenyliminodibromobenzoquinone* (*Pentabromo-*

quinoneanil),  (?), crystallises in very dark red needles with a bronze lustre; these needles are sometimes aggregated in stellate clusters, at other times they develop into well-formed prisms. It is readily soluble in chloroform, acetone, or benzene, and very sparingly so in acetic acid, alcohol, or petroleum. It is best crystallised from petroleum (b. p. 120°) or from a mixture of benzene and petroleum. On analysis:

0·1509 gave 0·1390 CO_2 and 0·0150 H_2O. $C = 25{\cdot}12$; $H = 1{\cdot}104$.
0·2107 ,, 0·3442 AgBr. $Br = 69{\cdot}35$.
0·3096 ,, 6·8 c.c. moist nitrogen at 8·8° and 748 mm. $N = 2{\cdot}625$.
$C_{12}H_4ONBr_5$ requires $C = 24{\cdot}92$; $H = 0{\cdot}7$; $N = 2{\cdot}43$; $Br = 69{\cdot}18$ per cent.

Pentabromoquinoneanil can be hydrolysed by dissolving in excess of concentrated sulphuric acid or by boiling with a 30 per cent. solution of sulphuric acid in acetic acid. In the latter case, a few minutes' boiling is necessary. On cautious addition of water, *s*-tribromoaniline separates in a nearly pure condition; the 2 : 6-dibromobenzoquinone can be extracted from the diluted mother liquor by means of chloroform or ether, and purified by crystallisation from dilute alcohol; it crystallised in golden-yellow plates melting at 122°, and did not lower the melting point of a specimen of 2 : 6-dibromoquinone.

2 : 4 : 6-*Tribromophenyl*-2′ : 6′-*dibromo*-4-*hydroxyphenylamine*,

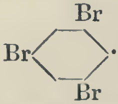
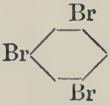
 (?).

—To a solution of the pure pentabromoquinoneanil (m. p. 171°) in acetone an equal weight of zinc dust was added, and glacial acetic acid was dropped in until the solution became colourless. After filtering, water was added, when a white solid, melting at 154°, separated; from its hot solution in petroleum it crystallised in clusters of long, silky needles melting at 155—156°:

0·1931 gave 0·3130 AgBr. $Br = 68{\cdot}96$.
$C_{12}H_6ONBr_5$ requires $Br = 68{\cdot}94$ per cent.

The pentabromohydroxydiphenylamine is readily soluble in chloroform, benzene, or alcohol, and moderately so in glacial acetic acid; in petroleum it is but sparingly soluble. Dilute aqueous sodium hydroxide dissolves it freely.

The hydroxydiphenylamine can be readily reconverted into the quinoneanil by oxidation with mercuric oxide in benzene solution, or by chromic acid in acetic acid solution.

2 : 4 : 6-*Tribromophenyliminotribromobenzoquinone* (*Hexabromoquinoneanil*) *and* 2 : 4 : 6-*Tribromophenyltribromo-4-hydroxyphenylamine*,  $\cdot N\colon C_6HBr_3\colon O$ and  $\cdot NH\cdot C_6HBr_3\cdot OH$.—The hexabromoquinoneanil was contained in the petroleum extracts of the original red solid. On recrystallising the material, which was obtained on evaporating this solution from petroleum, a substance was obtained melting at 143—144°. Further recrystallisation failed to change the melting point. Analysis showed that it was a mixture of the penta- and hexa-bromoquinoneanils; thus, bromine was found 70·61 and 70·74 per cent., whilst the pentabromo-derivative requires 69·18 and the hexabromo-derivative 73·04. A separation was only effected by reducing the quinoneanils to the corresponding hydroxydiphenylamines.

This reduction was carried out in the manner above described, by zinc dust in acetone solution. The hydroxydiphenylamines were precipitated by water from the acetone solution, and then extracted with small quantities of hot alcohol. A residue was left which melted at 195°; recrystallisation from chloroform or glacial acetic acid raised the melting point to 207°. Analysis showed that this was the pure hexabromohydroxydiphenylamine:

0·184 gave 0·1491 CO_2 and 0·0163 H_2O. $C = 22·1$; $H = 0·98$.

0·1935 gave 0·3304 AgBr. $Br = 72·66$.

$C_{12}H_5ONBr_6$ requires $C = 21·86$; $H = 0·77$; $Br = 72·82$ per cent.

This hexabromohydroxydiphenylamine is sparingly soluble in all solvents; it crystallises extremely well from chloroform in long, white, silky needles, and from glacial acetic acid in prisms. It dissolves freely in dilute aqueous sodium hydroxide.

The alcoholic extracts of the mixture of hydroxydiphenylamines yielded on evaporation a somewhat impure pentabromohydroxydiphenylamine; it was oxidised to the corresponding quinoneanil which, after one recrystallisation from petroleum, melted at 171°, the melting point of the pentabromoquinoneanil.

Hexabromoquinoneanil.—The hexabromohydroxydiphenylamine was converted into the corresponding quinoneanil in the following manner. 0·75 gram of the hydroxy-compound was suspended in 25 c.c. of pure benzene and a slight excess of yellow mercuric oxide added. On warming the mixture, the hydroxydiphenylamine slowly dissolved. For complete oxidation several hours warming is required. On the other hand it is inadvisable to use excess of mercuric oxide, as other changes are thereby induced. After filtering the solution, the quinoneanil is obtained in deep red, six-sided prisms on evaporation.

This oxidation can also be conveniently carried out with chromic acid in acetic acid solution. Owing to the insolubility of the hydroxydiphenylamine a large volume of solvent must be used. A slight excess of chromic acid dissolved in acetic acid is added to the solution of the hydroxydiphenylamine, the temperature being maintained at 20—30°; a higher temperature is to be avoided. On adding water, the quinoneanil crystallises in scarlet needles.

Hexabromoquinoneanil is more readily soluble in all solvents than the pentabromo-derivative. It crystallises in prisms when its solution in cold benzene is slowly evaporated, and in small aggregates of needles from its solution in hot petroleum. It is remarkable that the latter crystals are pale red, whilst the prisms are a deep port-wine colour. The compound melts at 134—135°:

0·15 gave 0·256 AgBr. Br = 72·61.

$C_{12}H_3ONBr_6$ requires Br = 73·04 per cent.

The authors wish to take this opportunity of expressing their thanks to the British Association and to the Chemical Society for grants which have partly defrayed the cost of this research.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

XV.—*The Affinity Constants of Aminocarboxylic and Aminosulphonic Acids as determined by the aid of Methyl-orange.*

By VICTOR HERBERT VELEY.

Introductory.

IN a former paper (*Zeit. physikal. Chem.*, 1906, 57, 147) on the above subject it was established that the affinity factors of organic acids experimentally found by a tintometer method were in complete accordance with those deduced by Ostwald and his co-workers by the electric conductivity method, in accordance with the well-known general equation:

$$\phi(k) = a^2/(1-a)V \qquad a = \mu/\mu_\infty \qquad (1)$$

The acids formerly investigated, namely the carboxylic, and certain hydroxy-, nitro-, and chloro-derivatives of the aliphatic and aromatic series, conformed to two general types, expressible by the equations :

$$\text{I.} \begin{cases} y = kx & (ia) \\ y = kx - b & (ib) \end{cases}$$

$$\text{II.} \quad \log y = \log k + x \log a \qquad \text{(ii)}$$

namely those of straight lines and logarithmic curves.

In the above equations y is the variable height of a column of a methyl-orange solution, x unit masses or volumes of acids added to a fixed similar column of the same methyl-orange solution, k the affinity factor. The constant b in equation (ib) depends on the conditions of each set of observations, and the constant x in equation (ii) is the number of unit masses of acid added less one. In the present communication this simple line of investigation is extended more particularly to the aminocarboxylic acids, generally regarded as true amphoteric electrolytes, and the aminosulphonic acids, a class of substances somewhat neglected from the physico-chemical standpoint, although herein of more importance, as the indicator methyl-orange belongs to them.

Method of Experiment.—This was precisely similar to that previously described, and consisted in adding successive portions of 0·1 c.c. of the several acid solutions to 20 c.c. of a $N/40,000$ methyl-orange solution contained in one tube of a tintometer, and varying the height of a column of the same solution contained in the other tube of the tintometer until the colour tints were equally matched. Improvements in the method of working might doubtless have been introduced, but as the investigation had been commenced somewhat hurriedly for the Sixth International Congress of Applied Chemistry at Rome, it was thought best to continue the work on the previous simple lines. Greater accuracy might have resulted from such improvements, such as a reduction of error from 5 to 3 per cent. or even less. However that may be, the results herein detailed conform in every way to those obtained in the past work, and even though the experimental error may be regarded as excessive, yet it is not greater than those deduced from electric conductivity experiments, wherein observational errors of a first power magnitude become, by the process of calculation, of a second power magnitude. It will be understood that if 0·1 c.c. of a x/N-solution of an acid is added to 20 c.c. of the standard methyl-orange solution, the concentration at the first observation is $x/200N$, and at the nth observation is $x/\frac{200}{n}N$. The reciprocals of these numbers, designated V, are expressed in equivalent acidic and not in molecular concentrations.

Samples of Acids.—Some of the samples were purchased from well-known firms specially for the investigation; others were kindly supplied from the laboratory collections of the University of Oxford and of Magdalen College, and by individual friends. I have to express my obligations for kindness shown, and herein especially to the Directors of the Badische Anilin- und Soda-Fabrik, who kindly presented me with a collection of aniline- and naphthylamine-sulphonic acids; my only regret is that some of the acids were found, owing to their sparing solubility, to be not very suitable for the purpose of the investigation.

Aminocarboxylic Acids—Amphoteric Electrolytes.

Within the last few years especial attention has been paid to this class of substances; it is only necessary to refer to the work of Winkelblech (*Zeit. physikal. Chem.*, 1901, **36**, 546), Bredig (*Zeit. Elektrochem.*, 1899, **6**, 34), and Walker (*Proc. Roy. Soc.*, 1904, **73**, 155, and 1904, **74**, 271) on the amino-acids (aliphatic and aromatic), and of Johnson (*Proc. Roy. Soc.*, 1906, **78**, 82 *et seq.*) and others on the methyl derivatives of the latter. (The special case of cacodylic acid, classed with the amphoteric electrolytes, will be considered separately.) In the above-mentioned investigations both the acidic and basic constants have been determined by various methods; in the present work only the former are studied, either as regards the acids themselves or their hydrochlorides.

Aliphatic Aminocarboxylic Acids.—Aminoacetic acid (glycine), a sample of which was originally purchased from Kahlbaum and recrystallised subsequently, gave no acid reaction, even with a solution of original concentration *N*/10 (compare Imbert and Astruc, *Compt. rend.*, 1900, **130**, 37); aminopropionic acid (alanine), originally purchased from Schuchardt, gave under the same conditions an acidity change too faint for accurate measurement; hydroxyphenylaminopropionic acid (tyrosine) also gave no reaction with a concentration approximately *N*/50, namely, at about the limit of its solubility in warm water. Thus, as regards their reaction with methyl-orange, the acidic and basic constants compensate one another.

Hydrochlorides of the above Acids.—As preliminary experiments showed that these substances reacted with methyl-orange, mainly as hydrochloric acid, the aminocarboxylic acid only producing a slight positive or negative effect according to its specific nature, results were obtained with hydrochloric acid itself for the purpose of comparison.

Hydrochloric Acid.—A standard solution, *N*/10, of this acid was prepared and its value ascertained by standard alkali; this solution was diluted to concentrations *N*/400, *N*/300, and *N*/200 respectively. The results obtained are given in Table I; V is the equivalent concentrations at the first observation, x the units of 0·1 c.c. added (V/x being the corresponding equivalent concentrations), and y the heights of the variable tintometer column expressed in centimetres. (In successive tables the x column will be omitted and taken to be understood.)

TABLE I.

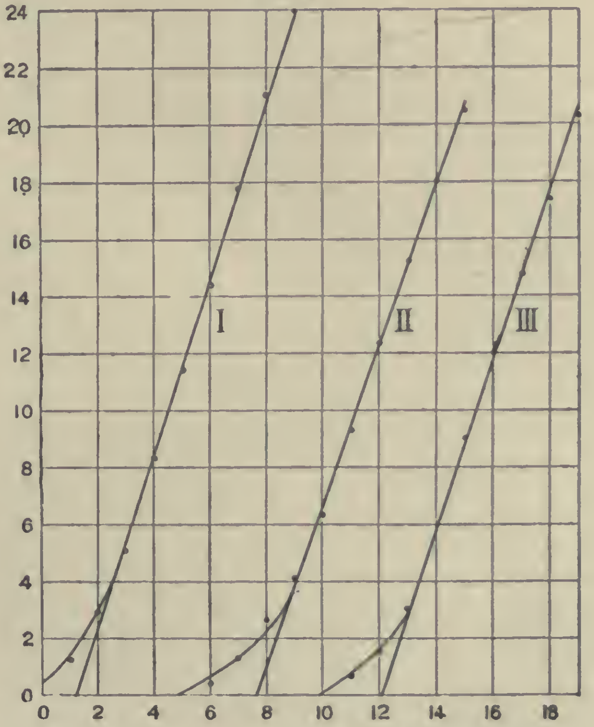
	$V=8\times10^4$.		$V=6\times10^4$.		$V=4\times10^4$.	
x.	y (found).	y (calc.).	y (found).	y (calc.).	y (found).	(y calc.).
1	0·6	—	0·9	—	1·35	—
2	1·2	—	2·4	—	2·85	—
3	2·1	—	4·2	—	5·1	5·2
4	3·9	—	8·3	8·3	8·4	8·3
5	5·1	5·1	10·5	10·7	11·4	11·4
6	6·6	6·6	12·9	13·1	14·4	14·5
7	8·4	8·1	15·6	15·5	17·7	17·6
8	10·2	9·6	18·0	17·9	21·0	20·7
9	11·4	11·1	20·9	20·3	24·0	23·8
10	12·9	12·6	—	—	26·7	26·9
11	14·1	14·1	—	—	—	—
12	15·3	15·6	—	—	—	—

If the results are set out graphically it appears that the first few observations (as bracketed) lie on a logarithmic curve, which does not pass through the origin of co-ordinates, but has the x axis as an asymptote (see I, Fig. 1, for series III). The remaining observations lie on straight lines of general equation $y=kx-b$ (cf. *supra*), the constants of which are for series I $k=1·5$, $b=2·4$, for series II $k=2·4$, $b=1·3$, for series III $k=3·1$, $b=4·1$. The constants k are thus in the ratios 1·5 : 2·4 : 3·1, whereas if referred to their original concentrations and expressed in terms of the first of them, taken as correct the ratios are 1·5 : 2·25 : 3·0. On comparing the found values of y with those calculated from the general equation, substituting the second constants, it is evident that, with one or two exceptions, the differences are well within the 5 per cent. admitted limit.

In no case was the reaction pushed to its extreme limit, as it has been found previously that the red ion of methyl-orange formed by addition of excess of mineral acid could not be matched by a variable column of methyl-orange solution, which contains only the orange or orange-red ion. As regards the curved portion the equations to the logarithmic curves are, so far as they can be determined by observations, few in number; for series I $y=(0·23)2^x$, for series II $y=(0·525)2^x$, for series III $y=(0·65)2^x$. The curved portion corresponds to some induction period; it may be idle to speculate on the matter, but a possible cause is the presence of ammoniacal compounds in the water used which set up an opposing reaction to the methyl-orange. In a former paper (*Proc. Roy. Soc.*, 1901, 69, 87) attention has been drawn to the persistent retention of some ammoniacal compound or compounds in distilled water, and more recently Burgess and Chapman (Trans., 1906, 89, 1414 *et seq.*) have found the well-known induction period of hydrogen and chlorine to be caused, *inter alia*, by the presence of ammonia or more probably complex ammoniacal compounds, albuminoses or the like. However this may be, since this induction period appeared in so many series of observations herein recorded, it is probably due to some common cause.

Glycine Hydrochloride.—A beautiful crystalline specimen of this substance was presented to me by Mr. J. E. Marsh, F.R.S. ; some of the crystals being of dimensions 14 × 8 mm. Mr. T. V. Barker, B.A., B.Sc., of the Mineralogical Department, Oxford, was kind enough to ascertain that the crystallographic axes and forms of the specimen, namely, orthorhomic, 1 : 1·1108 : 0·0309 ; forms, ∞P, $\infty \breve{P}_2$, $\infty \bar{P}\infty$, $\breve{P}\infty$, $\frac{1}{2}P\infty$; P ; hemihedral ; cleavage perfect, $11^e\frac{1}{2}\breve{P}\infty$, were identical with those given by Schwabus in a somewhat obscure publication (Vienna, 1855), partly reproduced in *Jahresber.*, 1854, 676.

Fig. 1.



Note as to Plates.—The ordinates represent the heights in centimetres of the variable methyl-orange column, the abscissæ the unit masses, or volumes of the acids added ; the origin is shifted for the Graphs II and III (Fig. I), and for II (Fig. II), for the better comparison and to avoid overlapping.

Two solutions of $N/150$ and $N/200$ concentration respectively were made up, which gave the results set out in Table II.

TABLE II.

$V=4\times10^4$.		$V=3\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·3 1·2 2·6	— — —	1·2 2·8	— 2·8
4·1	4·0	6·3	6·3
6·3	6·8	10·3	9·9
9·3	9·6	13·5	13·5
12·3	12·4	16·8	17·1
15·2	15·2	19·8	20·7
18·0	18·0	—	—
20·4	20·8	—	—

The results obtained are similar to those obtained from hydrochloric acid, the first few observations being upon a logarithmic curve, the remainder on a straight line $y=kx-b$ (compare I, Fig. 2, for series I). The values in the second and fourth columns are calculated by introducing constants $k=3·6$, $b=4·5$, and $k=2·8$, $b=7·2$. The constants k are in the ratio $2·8:3·6$, whereas if referred to original concentrations the ratio is $2·8:3·7$, a difference within experimental error. The equations to the logarithmic curves are $y=(0·3)2^x$ and $y=(0·75)2^x$, so far as it is possible to ascertain them.

Alanine Hydrochloride.—This substance was prepared by dissolving aminopropionic acid in such a volume of concentrated hydrochloric acid that the latter contained a slight excess of that required for equimolecular combination. The solution was spontaneously evaporated, the crystalline residue washed with absolute alcohol, redissolved in water, and the solution spontaneously evaporated over sulphuric acid. The crystalline magma was dried on a porous tile, and the minute crystals, owing to their deliquescent nature, dissolved as quickly as possible in the required quantity of water.

Only one set of experiments was conducted with this substance, as unfortunately within twenty-four hours of the preparation of an original solution a hypomycete had made a considerable growth therein.*

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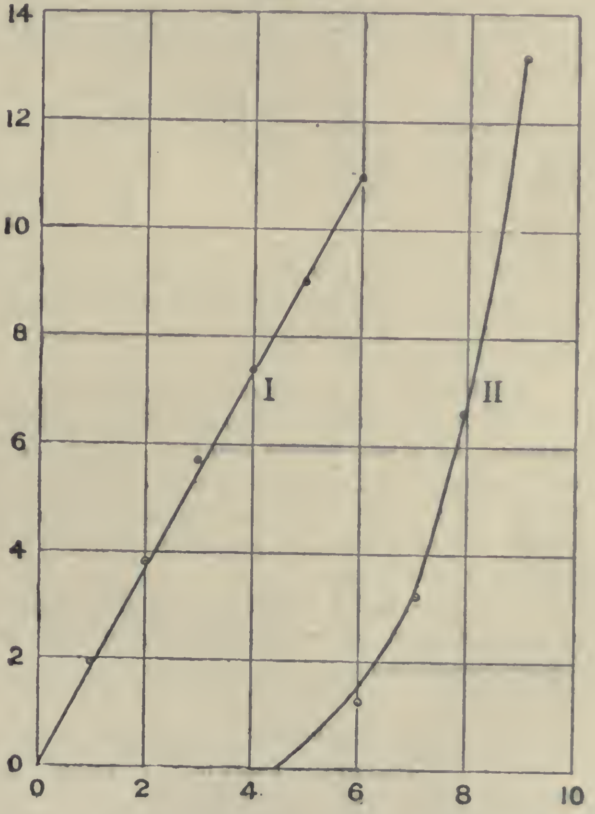
* Though wholly foreign to the present inquiry, yet it may be worthy of mention that these hydrochlorides of the amino-acids were found, from sad experience, to be most convenient media for the growth of such micro-organisms, doubtless as supplying carbon, amino-nitrogen, and chlorine; so far as I am aware the introduction of these substances in culture media has not been tried.

TABLE III.

$V=4\times10^4$.		$V=4\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·6	—	10·8	10·7
1·8	—	14·1	14·0
4·2	4·1	17·3	17·3
7·5	7·4	20·4	20·6

The figures in the second column are calculated from the equation $y=kx-b$, $k=3{\cdot}3$, $b=5{\cdot}8$; the results on the curved portion can be expressed by an equation $y=(0{\cdot}5)x^2$.

FIG. 2.



The behaviour of alanine hydrochloride is thus precisely similar to glycine hydrochloride.

Betaine Hydrochloride.—A sample of this substance was purchased from the Aktien-Gesellschaft für Anilin Fabrikation, Berlin, under the name of "Acidol," being a preparation for the internal administration of hydrochloric acid in a convenient form for certain gastric complaints. The preparation was recrystallised from cold water by spontaneous evaporation and its chlorine contents determined by the Volhard method:

Found, Cl = 23·09. Calculated, Cl = 23·1 per cent.

Solutions of original concentration $N/400$, $N/300$, and $N/200$, being equimolecular to those of hydrochloric acid (compare *supra*), were made up, and gave the results set out in Table IV.

TABLE IV.

$V = 8 \times 10^4$.		$V = 6 \times 10^4$.		$V = 4 \times 10^4$.	
y (found).	y (calc.)	y (found).	y (calc.).	y (found).	y (calc.).
0·9	—	0·6	—	0·6	—
1·5	—	1·2	—	1·5	—
2·7	2·7	3·0	2·9	3·1	2·8
4·2	4·2	4·9	4·7	5·9	5·8
5·6	5·7	7·2	7·1	9·0	8·8
7·2	7·2	9·0	9·2	12·0	11·8
8·7	8·7	11·1	11·3	14·7	14·8
10·2	10·2	13·2	13·4	17·4	17·8
				20·4	20·8

The numbers in the second, fourth, and sixth columns are calculated from the straight line equation, the values of k being taken as 1·5, 2·1, and 3, and those of b as 1·8, 3·4, and 6·2 respectively (compare I, Fig. 1, for series III).

Tyrosine Hydrochloride.—This substance was prepared according to the directions of Erlenmeyer and Lipp, and obtained in tufts of hard, glistening prisms. As it was further found, in accordance with the observations of these authors, that when excess of water is added to such crystals, tyrosine separates out, leaving a small portion, if any, of the salt dissolved in water, it was not possible to conduct any observations with methyl-orange solution.

General Conclusions.—In the following table the values of k for solutions of the same equivalent concentration are put together for the purpose of better comparison.

TABLE V.

	$V = 8 \times 10^4$.	$V = 6 \times 10$	$V = 4 \times 10^4$.	$V = 3 \times 10^4$.
Hydrochloric acid	1·5	2·4	3·1	—
Glycine hydrochloride...	—	—	2·8	3·6
Alanine hydrochloride..	—	—	3·3	—
Betaine hydrochloride...	1·5	2·1	3·0	—

Neglecting the result of alanine hydrochloride as possibly too high owing to the difficulty of obtaining this substance in a state of purity, the results of the remaining hydrochlorides of the amino-acids are very approximately equal to those of hydrochloric acid.

It would therefore appear that either (i) these hydrochlorides are hydrolysed completely, or nearly so, into the amino-acids and hydrochloric acid, or (ii) the methyl-orange, as a disturbing factor, nearly completely displaces the former from the latter.

The first hypothesis would seem at first sight to be in opposition to the experimental evidence of Bredig (*loc. cit.*) and Walker (*loc. cit.*), who found such hydrolysis to be partial and not complete.

But the concentrations in the different methods of inquiry were widely different; the most dilute solution used by the above observers equals $V=1024$ (approximately 10^3), whereas the most concentrated solution in my experiments equals $V=3\times10^4$, or thirty times more dilute. Thus the discrepancy may only be apparent and not real; further electric conductivity measurements with such dilute solutions could only solve the question.

The second hypothesis would involve the complete displacement of an aminosulphonic by an aminocarboxylic acid, although all results show that the former are more acidic and not more basic than the latter.

Aspartic Acid.—A sample of this acid was purchased from Kahlbaum and purified by recrystallisation.

The following results were obtained:

TABLE VI:

$V=4\times10^4$.	$V=3\times10^4$.	$V=2\times10^4$.
0·3	0·6	1·5
0·6	1·2	3·0
1·05	2·4	5·1
2·25	4·2	7·8
3·9	6·3	11·1
5·55	8·1	14·7

The above results, though few in number as the reaction is soon complete, are similar in type to those of hydrochloric acid, in that the first few observations are in accordance with the logarithmic expression $\log y=k+x\log a$, the remainder with the straight line expression $y=kx-b$, the values for k being 1·6, 2·0, and 3·1 respectively.

It appears remarkable that, firstly, aspartic acid, an aminocarboxylic acid, should behave as a strong mineral acid, and secondly, though the values of the initial period are less than those of succinic acid for the same concentration, yet in the corresponding straight line periods the value $k=1{\cdot}7$ of the former should be approximately three times greater than that of the latter, $k=0{\cdot}6$.

Aspartic acid has been studied by P. Walden (*Zeit. physikal. Chem.*, 1891, 8, 481) by the electric conductivity method, who found that as the values of V were increased in geometrical proportion, the values of

k, instead of being constant, increased approximately in arithmetical proportion, and also that the value of k for solutions of the same concentration were greater than those of succinic acid. This author obtained the following results.

V.	$K = k \times 10^2$.	Differences.
32	0·0067	—
64	0·0079	12
128	0·0094	15
256	0·0109	15
512	0·0122	13
1024	0·0137	15

The above results are expressible by a general formula, $k = a + b \log V$, or actually $k = 0{\cdot}0067 + (0{\cdot}0014/\log 2) \log V$.

Although it seems hardly possible to accept the hypothesis of Walden that this result is conditioned by the formation of an inner anhydride, $CO_2H{\cdot}CH_2{\cdot}CH{<}\begin{matrix}NH\\|\\CO\end{matrix}$, as this would, from the analogy of betaines, increase the basic function; although also the abnormality of this acid might be due to the presence of an asymmetrical carbon atom associated with groupings which could not compensate one another, yet it is a matter of special interest that the results obtained by the methyl-orange tintometer method proceed on parallel lines to those obtained by the electric conductivity telephone method.

Cacodylic Acid, $(CH_3)_2AsO(OH)$.—This acid is here introduced as intermediate as regards its acidic function between the amino-carboxylic acids of the aliphatic and those of the aromatic series.

During the past few years considerable discussion has taken place as to whether this acid can be truly classed among amphoteric electrolytes; the literature has been collated by Johnson (*Ber.*, 1903, **37**, 3625). It was shown by Imbert (*Compt. rend.*, 1899, **129**, 1244) that this acid is neutral towards alkalis with methyl-orange as an indicator, but it behaves as a monobasic acid with phenolphthalein as indicator, an observation confirmed by Zawidski (*Ber.*, 1904, **36**, 3325). On the other hand, the values of k by the electric conductivity method obtained by different observers, although not concordant among themselves, nor even concordant with the same observer for different concentrations, yet so far agree in showing that the value is of an order corresponding to that of a true amphoteric electrolyte; this result is also confirmed by independent observations by the hydrolysis method.

It seemed, therefore, of interest to study the behaviour of this acid by the methyl-orange method notwithstanding the above statement of Imbert, who, apparently, used the indicator according to the usual practice of volumetric analysis.

As the sample, purchased from Kahlbaum, was in the form of well-developed crystals, it was considered unnecessary to purify it further.

The following series of observations were made, of which two were conducted at one time with solutions from one stock, and the third after the interval of some weeks from another stock.

TABLE VII.

$V=2\times10^3$.	$V=1\times10^3$.	$V=5\times10^3$.
0·75	1·5	3
1·5	3·3	6
2·25	4·8	9·1
3·0	6·3	11·9
3·75	7·5	—
4·5	—	—

It will be readily apparent that the results are all in accordance with the straight line formula $y=kx$, the values of k being 3, 1·55, and 0·75 respectively, namely, in the same ratio as their concentrations 4 : 2 : 1, and also by this method of experiment cacodylic acid has a higher acidity value than the aminocarboxylic acids of the aliphatic series, which gave no appreciable reaction with dilution $v=2\times10^3$, but a lower value than the corresponding acids of the aromatic series (see below). Cacodylic acid would therefore be rightly classed among true amphoteric electrolytes.

Aminocarboxylic Acids (Aromatic).

Aminobenzoic Acids.—As regards the reactions of these acids with methyl-orange, Imbert and Astruc (*loc. cit.*) observed that the 1 : 2- and 1 : 3-acids are scarcely neutral, but the 1 : 4-acid is sensibly acid.

All three isomerides were investigated; two of them the 1 : 3- and 1 : 4-acids were laboratory preparations, the third or 1 : 2-acid was purchased from Kahlbaum; all were purified by recrystallisation.

It was found that these acids differed from the aminoacetic acids in possessing a distinct acid function, although the reaction soon came to an end. The following results were obtained :

TABLE VIII.

Acid.	$V=1\times10^4$.	$V=2\times10^4$.	$V=4\times10^4$.
1 : 2	3·1	1·65	0·85
	6·2	3·30	1·7
	—	—	2·53
1 : 3	3·6	1·8	0·9
	7·2	3·6	1·8
	—	5·4	2·7
1 : 4	—	2·2	1·2
	—	4·6	2·4
	—	6·5	3·6

The above results, though few in number on account of the nature of the case, are all in accordance with the straight line formula $y=kx$, the values being the highest for the 1 : 4- and lowest for the 1 : 2-acid.

The results are in general accordance, not only with the qualitative observations of Imbert and Astruc, but also with the conductivity measurements of Ostwald and Winkelblech, which have recently been discussed by Walker in connexion with his theory of amphoteric electrolytes. It may be of interest to compare the conductivity results of Winkelblech as set forth by Walker, and my results at the greatest dilutions only in each case:

TABLE IX.

Acid.	Winkelblech. $Ko \times 10^5$ ($V=1024$).	Veley. K($V=4 \times 10^4$).
1 : 2	0·96	0·85
1 : 3	1·07	0·90
1 : 4	1·17	1·2

The magnitudes are of a precisely similar order, the variations from a strict arithmetical ratio being such as might be expected by the application of methods so widely different.

Oxanilic Acid.—This acid may conveniently be considered here; the sample used was a laboratory preparation, which was purified by recrystallisation. The following results were obtained, and in the table the top figures in the third and fourth columns follow on from the bottom figure in the first and second columns respectively:

TABLE X. $V=4 \times 10^4$.

I. Found.	II. Calc.	III. Found.	IV. Calc.
1·5	1·5	10·8	10·5
2·9	3·0	12·3	12·0
4·5	4·5	13·8	13·5
6·0	6·0	15·6	15·0
7·4	7·5	17·7	16·5
9·0	9·0	19·8	18·0

The values given in the second and fourth column are calculated from the straight line formula $y=kx$ ($k=1·5$); it will be observed that although at first the difference $y'-y$ is constant, namely, 1·5, yet towards the end there is a marked tendency for this difference to increase. Its behaviour is quite analogous to that of other acids, which likewise show an increase of electric conductivity factor $(\phi)k$ with increase of dilution.

Saccharin (*Benzoicsulphinimide*).—Although this substance is not strictly an acid, but an imide, yet as it has been shown that it resembles acids in accelerating the decomposition of ammonium nitrite (Trans., 1903, 83, 747), being probably converted into the corresponding acid, $SO_3H\cdot C_6H_4\cdot CO\cdot NH_2$, on hydrolysis (a reaction which takes place on the digestive tract), it was thought worthy of interest to study its behaviour as containing a sulphonic and carboxylic grouping.

The sample, originally purchased from Merck, was purified by recrystallisation, and the results obtained were as follows:

TABLE XI.

$V=8\times10^4$.		$V=4\times10^4$.	
y (found).	*y* (calc).	*y* (found).	*y* (calc.).
1·2	1·7	2·6	2·7
2·7	2·7	5·4	5·4
4·0	4·1	10 9	10·8
5·4	5·4	,,	,,
7·8	7·6	,,	,,
10·8	10·8	,,	,,

In both cases the values of *y* are calculated from the logarithmic equation $\log y=\log k+x\log a$, in which the values of *k* are 1·9 and 2·7, and of *a* are 1·41 and 2·0 respectively.

It would appear from the above results that saccharin on hydrolysis gives an acid with a sulphonic and not a carboxylic grouping, since towards methyl-orange it behaves when in solution as an acid of high acidic function, resembling formic and oxalic acids.

Aminosulphonic Acids.

Hitherto the affinity constants of these substances has been determined mainly by the electric conductivity method, partly by Ostwald (*Zeit. physikal. Chem.*, 1889, 3, 406 *et seq.*), and more fully by Ebersbach (*ibid.*, 1893, 11, 608), and it has been shown generally that the magnitudes of these constants are of a higher order than the aminocarboxylic acids; the aminosulphonic acids are not therefore usually classed among the true amphoteric electrolytes, from which they differ in other important respects.

Anilinemonosulphonic Acids.—Two out of the three isomeric modifications were investigated, namely, the 1 : 4 or sulphanilic acid (two specimens, one a laboratory sample, and the other purchased from Kahlbaum), both of which were purified by recrystallisation, and the 1 : 3 or metanilic acid, supplied by the Badische Anilin- und Soda-Fabrik, also recrystallised.

Metanilic Acid.—The following results were obtained:

TABLE XII.

$V=4\times10^4$.	$V=2\times10^4$.	$V=4\times10^4$.	$V=2\times10^4$.
1·95	3·8	7·4	16·3
3·8	8·0	9·0	20·8
5·7	12·0	10·8	—

The results in both cases are in accordance with the straight line expression $y=kx$, the values of k being 1·85 and 4 respectively, the ratio of the numbers being that of their concentrations within the 5 per cent. error.

Sulphanilic Acid.

As the two samples, alluded to above, gave identical results, those obtained from one only of them are given:

TABLE XIII.

$V=8\times10^4$.		$V=4\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·6	1·05	1·2	1·65
1·5	1·5	3·2	3·3
2·3	2·2	6·6	6·6
3·3	3·2	13·2	13·2
4·9	4·6	,,	,,
6·7	6·7	,,	,,
9·3	9·6	,,	,,
13·8	13·9	,,	,,

The results given in the second and fourth columns are calculated from the logarithmic expression $\log y=\log k+x\log a$, the values for k being taken as 1·05 and 1·65 and of a 1·45 and 2·0 respectively. It appears remarkable that of these isomerides one should conform to the straight line and the other to the logarithmic expression; the results for the same concentration are set out graphically in curve II (figs. 1 and 2). Ostwald (*loc. cit.*) found that both the 1 : 3- and 1 : 4-acids gave regular results, although the value of k for the former was about three times greater than for the latter (actually 0·0581 : 0·0181). However this may be, it will be shown in the sequel that such a difference in behaviour of isomeric aminosulphonic acids is not unique.

Anilinedisulphonic Acids.—Only one of the possible isomeric modifications was investigated, namely, the 1 : 2 : 4-acid, supplied by the Badische Anilin- und Soda-Fabrik. The sample was purified by dissolving in hot water, filtering through animal charcoal, crystallising, and drying the crystals on a porous tile; in this way a white specimen was obtained. As a sufficiently marked reaction was not produced with $N/100$ original solution (V being thereby 1×10^4), a solution which gave $V=0·75\times10^4$ was used, and the following results were obtained:

TABLE XIV.

$V = 0{\cdot}75 \times 10^4$.

y (found).	y (calc.).
1·5	1·5
3·2	3·0
6·3	6·0
11·9	12·0

The values given in the second column are calculated from the formula $\log y = \log k + x \log a$ ($k = 1{\cdot}5$, $a = 2$). It is evident that the introduction of a second SO_3H grouping into the 1 : 4-anilinesulphonic acid decreases rather than increases the affinity constant or acidic function.

As the same conclusion is arrived at, not only by electric conductivity results, but also by my results to be described in the sequel, it will not be necessary to consider further a matter so contrary to previously formed conceptions.

The Naphthylaminesulphonic Acids.—I was advised by Prof. Bernthsen, the Director of the Laboratory of the Badische Anilin- und Soda-Fabrik, that although the preparations were moderately pure, yet for the purpose of physico-chemical investigations they should be purified by recrystallisation.

Unless otherwise stated these preparations were purified by one or more recrystallisations from water.

a-*Naphthylaminemonosulphonic Acids.*

The 1 : 2-*Acid.*—As it was found that this sample contained some of its sodium salt, being doubtless derived from the corresponding salt of the 1 : 4-acid from which it was prepared, and did not give homogeneous crystals by the process above described, the original material was digested with dilute hydrochloric acid for two days, the coloured liquid drained off, and the residue washed with cold water until the washings gave no precipitate of silver chloride on addition of solution of the nitrate. The residue was then treated by the usual process, and, after a considerable but unavoidable waste of material, pale pink crystals were obtained, which appeared quite homogeneous when examined under the microscope.

The following results were obtained :

TABLE XV.

$V = 8 \times 10^4$.		$V = 4 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
1·2	—	0·75	—
1·8		1·5	
3·0	3·0	2·7	
5·4	5·5	5·1	4·8
8·4	8·0	9·3	9·4
—	—	14·4	14·0
—	—	18·0	18·6

The above results are less satisfactory than those obtained in any other set of observations, and it is thought possible that some secondary change might intervene at the outset as the tint produced, on addition of the successive portions of the acid to the methyl-orange solution, only assumed its final shade after standing for some minutes, and not immediately as in other cases.

But notwithstanding the imperfections, from whatever cause they may arise, the results are sufficient to show that this acid behaves as a strong acid (hydrochloric acid, for example), in that the first few results conform approximately to the logarithmic expression and the remainder to the straight line expression $y = kx - b$. (The results given in the second and fourth columns are calculated from constants $k = 2·5$ and $4·6$, $b = 4·5$ and $13·6$.)

The results are in accordance with those obtained by Ebersbach by the conductivity method, who found values for k varying from 2·23 ($V = 64$) to 1·09 ($V = 2048$); whether the former or the latter of these numbers or the mean thereof be taken, yet the value is five to fifty times greater than that found for any other naphthylaminesulphonic acid, and is of the order of magnitude corresponding to that of a nitro-aromatic acid. The point will be further discussed in the sequel.

The 1 : 4-*acid* was not sufficiently soluble in water for the purpose of this investigation.

The 1 : 5-*acid* gave a pale pink solution with slight * blue fluorescence when dissolved in water, but owing to its sparing solubility it was difficult to work with, and only one set of observations was made :

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* Wherever here, or in the sequel, the word "slight" is applied to the fluorescence, it will be taken to mean the appearance of the solutions under the conditions of ordinary daylight; when the beam of an electric arc is projected through such solutions the effect produced is quite magnificent.

TABLE XVI. $V=4\times10^4$.

$V=10^4$.	
y (found).	y (calc.).
1·0	1·12
2·4	2·25
4·5	4·5

The results in the second column are calculated from the expression $\log y=\log 1{\cdot}12+x\log 2$.

The 1 : 6-*acid* dissolved in water to give a pale pink solution; the following results were obtained :

TABLE XVII.

$V=8\times10^4$.		$V=4\times10^4$.		$V=2\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).	y (found).	y (calc.).
0·63	0·7	1·2	1·42	2·8	2·8
1·27	1·4	2·8	2·85	6·0	5·6
2·55	2·8	5·7	5·7	11·1	11·2
5·1	5·6	11·4	11·4	19·2	22·4

The values in the second, fourth, and sixth columns are calculated from the expression $\log y=\log k+x\log 2$ ($k=0{\cdot}7$, 1·42, and 2·8); the last observation in the 2×10^4 series is rather low, but it was evident on repetition that the possible reaction was nearly complete.

The 1 : 7-*acid* dissolved in water to give a pale pink solution with a faint blue fluorescence; the following results were obtained :

TABLE XVIII.

$V=8\times10^4$.		$V=4\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·6	0·6	0·9	1·25
1·2	1·2	2·4	2·5
2·4	2·4	4·95	5·0
—	—	9·9	10·0

The values in the second and fourth columns are calculated as above ($k=0{\cdot}6$ and 1·25 respectively), and it is evident from the figures given that the 1 : 7-acid is slightly weaker than the 1 : 6-acid.

Ebersbach's results showed that the 1 : 7-acid was slightly stronger than the 1 : 6-acid ($k=0{\cdot}0227$ and 0·0195 respectively).

The 1 : 8-*acid*, although obtained in a perfectly homogeneous crystal, showed no acid function whatever, even when added in very considerable excess to the methyl-orange solution. This result will be further discussed, but it is in accordance with Ebersbach's result, who obtained a value of $k=0{\cdot}001$ in round figures, one-twentieth of the values of the 1 : 6- or 1 : 7-acids.

β-Naphthylaminesulphonic Acids.

The 2 : 1-*acid* was obtained in pale pink prismatic needles; its solutions gave the following results:

TABLE XIX.

$V=8\times10^4$.		$V=4\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·3	0·5	1·05	1·15
0·9	1·0	2·1	2·3
2·25	2·0	4·8	4·6
4·2	4·0	9·6	9·2
8·1	8·0	18·6	18·4

The values in the second and fourth columns are calculated as above ($k=0{\cdot}5$ and 1·15, $a=2$ respectively); the k constants are not widely different from those of the 1 : 7-acid, although the reaction proceeds further. The electric conductivity constant has apparently not been determined.

The 2 : 5-*acid* was obtained as a fine crystalline powder; its solutions gave the following results:

TABLE XX.

$V=8\times10^4$.		$V=4\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·9	0·75	1·5	1·45
1·5	1·5	3·0	2·9
2·85	3·0	6·0	5·8
—	—	11·4	11·6

The values for k are taken as 0·75 and 1·45 respectively; it will be observed that though they are both higher than those of the 2 : 1-acid, yet the possible reaction sooner came to an end.

The 2 : 6-*acid* was not sufficiently soluble for the purpose of investigation.

The 2 : 7-*acid* was obtained in pale pink needles; owing to its sparing solubility only one set of observations was made and the solution kept warm for the purpose. The results are given below:

TABLE XXI.

$V=4\times10^4$.	
y (found).	y (calc.).
1·2	1·15
2·4	2·3
4·5	4·6

The value of $k = 1{\cdot}15$ is identical with that of the 2 : 1-acid at the same concentration, but all reaction sooner comes to an end.

The 2 : 8-*acid* was not sufficiently soluble for quantitative determinations, but it was proved that even on addition of a considerable quantity of a supersaturated solution to the methyl-orange no change was produced; the acid therefore resembles the 1 : 8-acid in showing no acidic function whatever.

Dimethyl-2-naphthylamine-8-sulphonic Acid.—I am greatly indebted to Dr. C. Smith for a sample (about 1 gram) of the above acid prepared and described by him (Trans., 1906, **89**, 1508); as sent it was in the form of crystalline (acicular needles) powder.

When dissolved in water at 25°, so as to give a $N/10$ solution, the liquid was of a pale yellow colour, but more dilute solutions displayed a beautiful pale blue fluorescence, so that their appearance somewhat resembled a very dilute solution of copper sulphate.

As the $N/10$ solution gave an immediate acid reaction with the methyl-orange solution it was further diluted, and the following results obtained:

TABLE XXII.

$V = 8 \times 10^4$.		$V = 6 \times 10^4$.		$V = 4 \times 10^4$.		$V = 2 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc).	y (found).	y (calc.).	y (found).	y (calc.).
0·7	0·65	0·9	0·9	1·2	1·35	2·7	2·75
1·2	1·3	1·8	1·8	2·7	2·7	6·0	5·5
—	—	3·7	3·6	5·4	5·4	10·8	11·0

Although the above acid differs from the other naphthylamine-mono- and di-sulphonic acids (see below), which contain an SO_3H grouping in the 8-position, in that it shows an acid reaction with methyl-orange, and although also the values of k in the expression $\log y = \log k + x \log 2$ ($k = 0{\cdot}65$, $0{\cdot}9$, $1{\cdot}35$, $2{\cdot}75$) are between the values found for the 2 : 1- and 2 : 5-naphthylaminesulphonic acids, yet all possible reaction sooner comes to an end. The results for the most dilute solution (8×10^4) are almost too small for accurate measurement; they have been quoted, not as of much import, but as of concordant arithmetical ratio with the remaining series.

However, the results are in perfect concordance with those obtained by the electric conductivity method in the case of the benzenoid aminosulphonic acids, which have shown that the substitution of hydrogen by methyl in the NH_2 grouping increases the value of k. The following illustrative examples are taken from the papers of Ostwald and Ebersbach (*loc. cit.*):

		k.			k.
$NH_2{\cdot}C_6H_4{\cdot}SO_3H$	(1 : 4)	0·0586	$NH_2{\cdot}C_6H_4{\cdot}SO_3H$	(1 : 3)	0·0185
$NHMe{\cdot}C_6H_4{\cdot}SO_3H$	,,	0·0666	$NMe_2{\cdot}C_6H_4{\cdot}SO_3H$	,,	0·037

Opportunity was taken to determine certain other physical data of the 2 : 8-dimethylaminosulphonic acid, namely the density of the $N/10$ solution, the solubility in water, and the degree of fluorescence. The following results were obtained: D^{15}_{15} (solution at or about its maximum saturation) $= 1·0073$; $D^{25}_{25} = 1·0058$; the weighings were corrected to a vacuum, and the thermometer corrected according to the Reichsanstalt methods.

Solubility S (grams in 100 grams water at 25°) $= 3·47$.

The blue fluorescence described by Dr. C. Smith is very remarkable; in ordinary daylight, under certain conditions, it is visible with a solution of concentration of the order of $N/2 \times 10^5$, or nearly one part in a million.

When a solution of the acid is allowed to evaporate spontaneously, well-formed transparent crystals separate, but at present they have not been obtained of sufficient dimensions for accurate crystallographic measurement.

a-Naphthylaminedisulphonic Acids.

Acids derived from the 1 : 4-*monosulphonic Acid.—The* 1 : 4 : 2-*acid*, obtained as a white, crystalline powder, dissolved in water giving a pale pink solution with a purple-blue fluorescence.

Two series of observations were made:

TABLE XXIII.

$V = 1 \times 10^4$.	$V = 0·5 \times 10^4$.
0·9	2·1
1·8	4·2
2·7	6·1
3·6	8·4
4·5	10·5
5·4	12·6
6·3	14·7
7·2	16·5
8·1	—

This disulphonic acid is remarkable in that, firstly, it was necessary to use more concentrated solutions to obtain observations, and, secondly, of all the mono- and di-naphthylaminesulphonic acids examined this is distinguished from the rest in giving results which conform to the straight line expression $y = kx$ ($k = 0·9$ and $2·1$); in this respect it resembles metanilic acid. The introduction of a second sulphonic grouping in this as in other cases diminishes rather than increases the acidic function.

The 1 : 4 : 6-*acid* was a white, crystalline powder, giving a nearly colourless solution with a pale blue fluorescence. The following results were obtained:

TABLE XXIV.

$V=4\times10^4$.		$V=2\times10^4$.		$V=1{\cdot}5\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).	y (found).	y (calc.).
0·6	0·6	1·2	1·35	1·9	1·9
1·5	1·2	2·7	2·7	4·2	3·8
2·4	2·4	5·4	5·4	7·5	7·6
4·8	4·8	10·9	10·8	—	—

The results are in accordance with the logarithmic expression ($k=0{\cdot}6$, $1{\cdot}35$, $1{\cdot}9$, $a=2$).

The 1 : 4 : 7-*acid*, obtained as a slightly deliquescent white powder, became slightly discoloured when dried at 80°.

The results were as follows:

TABLE XXV.

$V=4\times10^4$.		$V=2\times10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·6	0·6	1·2	1·3
1·2	1·2	2·7	2·6
2·1	2·4	5·4	5·2

The values found are practically identical with those of the 1 : 4 : 6-acid, although the reaction sooner comes to an end.

The 1 : 4 : 8-*acid* was obtained in yellowish-pink tabular crystals giving a yellow solution with faint fluorescence.

The acid reaction, even with original solution $N/10$, was almost inappreciable, and thus in terms of the other acids its effect may be considered *nil*.

The 1 : 5 : 7 (?)-*acid* (Badische Anilin- und Soda- Fabrik, D.R.-P. 69555) is prepared by sulphonating aceto-α-naphthalide or its 1 : 5-sulphonic acid and hydrolysing the acetyl compound with dilute sulphuric acid. The 7-position of the sulphonic-grouping appears to be doubtful. The sample sent was purified by allowing a cold-water solution to evaporate spontaneously; pale yellow needles separated, which rapidly effloresced.

A solution of original concentration $N/25$ gave no acid reaction with methyl-orange even on addition of excess. Therefore this acid behaves as acids which contain a sulphonic grouping in the 8-position. But so long as the constitution of the acid remains a matter of doubt, it does not appear desirable to draw any conclusion.

The β-Naphthylaminedisulphonic Acids.

The 2 : 3 : 6-*acid* was obtained partly as colourless, glassy plates, which rapidly effloresced, partly as a pale pink amorphous powder; by a process of rapid evaporation it was obtained in the latter form only. The acid probably, therefore, occurs in a labile crystalline and a stable, amorphous modification, but the conditions under which one or the other is formed have not as yet been accurately ascertained. The solutions showed a purple-blue fluorescence. Two series of observations were made with the following results:

TABLE XXVI.

$V = 4 \times 10^4$.		$V = 2 \times 10^4$.	
y (found).	y (calc.).	y (found).	y (calc.).
0·6	0·65	1·2	1·25
1·5	1·3	2·6	2·5
2·4	2·6	5·1	5·0
—	—	9·9	10·0

The values for k are not widely different from those obtained for the 1 : 4 : 7-acid.

The 2 : 6 : 8-*acid* gave no reaction with an original solution $N/50$, even when added in excess; hence relatively its effect may be regarded as *nil.*

General Conclusions regarding the Naphthylaminesulphonic Acids.

On reviewing the results obtained with these acids, two general facts come into prominence: namely (1) the positions 2 and to a less extent 7 afford cases of steric "furtherance,"[*] and (2) the position 8 affords a case of steric "hindrance."

As regards the steric hindrance effected by the 8-position, my observations are quite in accordance with those of Hewitt and Mitchell, as also of C. Smith (*loc. cit.*), in their studies on the reaction of various naphthalene derivatives with diazonium salts. On the other hand, as regards the steric furtherance of the 2-position my observations are in accordance with the results of Ebersbach. At present there do not appear to be many data as to the effect produced by the 7-position, relative to the positions 1 and 2.

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[*] As the phrase "steric hindrance" has now come into chemical literature, I have ventured to use the old Saxon word "furtherance" as its opposite. It appears that the noun has been used in this sense since 1440 (*York Mystery Play*), and the verb so far back as 888 (*Ælfred Chron.*). Perhaps I may raise a plea for the use of Saxon words, rather than those derived from Greek or Latin, separately, or even worse, conjointly.

Summary.

(i) The method of determining the affinity constants of acids by means of a dilute methyl-orange solution and a tintometer, formerly applied to the carboxylic acids and certain chloro- and hydroxy-derivatives, has been extended to the amino-carboxylic and sulphonic acids. It is shown that the same general mathematical expressions hold good, namely, those of straight lines, or logarithmic curves.

(ii) Acids which show irregularities in the Ostwald electric conductivity expression $\phi(k) = a^2/(1-a)V$ show similar irregularities in the methyl-orange method.

(iii) The aliphatic aminocarboxylic acids act as neutral substances, but their hydrochlorides as hydrochloric acid only, hydrolysis being nearly complete at the degree of dilution used.

(iv) The special cases of aspartic and cacodylic acids have been investigated.

(v) The aminobenzoic acids show a distinct acid function, and the factors obtained are in a similar arithmetical ratio to those deduced by Winkelblech at a different degree of dilution of the electric conductivity method.

(vi) The two aminobenzenemonosulphonic acids studied, namely, sulphanilic (1 : 4) and metanilic (1 : 3) acids, are remarkable in that the latter conforms to the straight line, but the former to the logarithmic expression. The introduction of a second sulphonic-grouping reduces rather than increases the acid function.

(vii) The study of the naphthylaminemono- and di-sulphonic acids affords examples of steric furtherance as regards the positions 2 and 7 and of steric hindrance as regards the position 8.

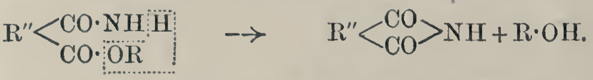
Lastly, I desire to express my thanks to Prof. Wm. Esson for assistance in the mathematical portion, and again to my colleagues at home and abroad for having kindly supplied me with such a wealth of material, without which this investigation could not have been completed.

XVI.—*Tetraketopiperazine.*

By Alfred Theophilus de Mouilpied and Alexander Rule.

The formation of ring compounds by the action of sodium alkyloxides on various phenylglycinoacetic esters has been investigated by one of us (*Ber.*, 1900, **33**, 2467; Trans., 1905, **87**, 435). The ease with which alcohol is eliminated in these cases has led us to apply the reaction to esters of the type of ethyl oxamate, in the hope that by the elimination of a molecule of alcohol between an ·OR group and an ·NH_2 group, ring compounds containing an imino-group might be produced.

In general, the reaction might be expected to be as follows:

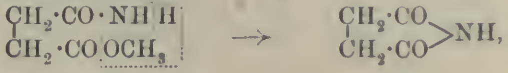


$$R''<\begin{matrix}CO\cdot NH\boxed{H}\\ CO\cdot\boxed{OR}\end{matrix} \longrightarrow R''<\begin{matrix}CO\\ CO\end{matrix}>NH + R\cdot OH.$$

Ethyl oxamate would by such a reaction give rise to the three-membered cyclic compound, oxalimide, $\begin{matrix}CO\\ | \\ CO\end{matrix}>NH$, the existence of which has not yet been clearly established. The only reference to this compound is in a paper by Ost and Mente (*Ber.*, 1886, **19**, 3228). The authors describe the preparation of oxalimide from oxamic acid by the action of phosphorus pentachloride, the yield being very small. It is described as crystallising in colourless, well developed monoclinic prisms. No reference is made to the melting point, and the results of analysis given apply equally well to a substance with twice the molecular weight, such as tetraketopiperazine. On boiling with water, the substance decomposed into oxamide and oxalic acid, and Ost and Mente thought it might be dioxaldiamide, $\begin{matrix}CO\cdot NH\cdot CO\\ | \qquad\quad |\\ CO\cdot NH\cdot CO\end{matrix}$, but they rejected this hypothesis on the ground that such a compound ought on hydrolysis to yield equal molecules of oxamide and oxalic acid, which they found not to be the case. This, however, is not to be expected, as any oxamide formed by the hydrolysis of the parent substance would, in its turn, be equally liable to saponification to oxamic and oxalic acids. We found that during hydrolysis of tetraketopiperazine, ammonia was evolved, and that the relative proportions of the products depended on the time of reaction and on the concentration of the hydrolyser.

Ost and Mente supposed that the simple oxalimide was obtained by them and that this reacted with water to form oxalic acid and ammonia; the latter then reacted with more oxalimide to form oxamide. It seems improbable that a compound of the configuration of oxalimide would have the stability ascribed to it by these authors. The present paper contains an account of the preparation and properties of tetraketopiperazine, and there seems to be but little doubt that this is the substance which they obtained and which is described in text-books as oxalimide. Further, their work has recently been repeated,* and no trace of either oxalimide or tetraketopiperazine could be detected.

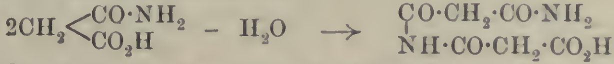
We first applied our method to methyl succinamate; this, on treatment with sodium alkyloxide in benzene solution, lost a molecule of alcohol and gave succinimide,



$$\begin{array}{l}CH_2\cdot CO\cdot NH\,H \\ | \\ CH_2\cdot CO\,OCH_3\end{array} \longrightarrow \begin{array}{l}CH_2\cdot CO \\ | \\ CH_2\cdot CO\end{array}\!\!>NH,$$

although in no great quantity.

In the case of ethyl malonamate, no ring formation took place as far as the main reaction is concerned, but the preferential saponification of the carboxyalkyl group in regard to the amino-group was brought about. Malonamic acid was not, however, isolated, but an acid resulting from the loss of one molecule of water from two molecules of the malonamic acid:



$$2CH_2<\begin{array}{l}CO\cdot NH_2 \\ CO_2H\end{array} - H_2O \longrightarrow \begin{array}{l}CO\cdot CH_2\cdot CO\cdot NH_2 \\ | \\ NH\cdot CO\cdot CH_2\cdot CO_2H\end{array}.$$

The use of theoretical amounts of sodium alkyloxides in dry benzene solutions seems to be a method of general application for the preferential saponification of carboxyalkyl groups occurring in the same compound with acid amide groups. In the ordinary way, a $\cdot CO\cdot NH_2$ group is readily saponified by alkali and always more easily than an accompanying $\cdot CO_2R$ group. Thus, in the case of ethyl oxamate, treatment with caustic soda causes an evolution of ammonia in the cold. Using the theoretical amount of sodium ethoxide in benzene solution, a good yield of sodium oxamate is obtained. We believe this method will be found to be of general application. In addition to oxamic acid, the latter reaction yields, after treatment with water, filtration and acidification with hydrochloric acid, a substance which analysis showed to have the formula $C_4H_2O_4N_2$ and a molecular weight of 142. This is the dioxaldiamide of Ost and Mente, or tetraketopiperazine. A better yield is obtained if ethyl oxamate is treated directly with the theoretical amount of sodium ethoxide in absence of benzene. We have also obtained the substance by the condensation of oxamide with ethyl oxalate in presence of sodium ethoxide:

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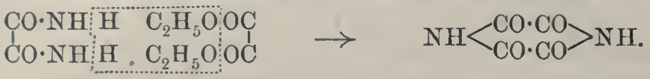
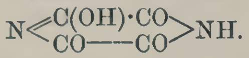
* The work has been carried out in these laboratories by Dr. A. W. Titherley and Dr. A. A. Hall in connexion with the attempted synthesis of oxalimide, and they inform us that their results were entirely negative.



$$\begin{array}{l} \mathrm{CO\cdot NH}\;\mathrm{H}\quad \mathrm{C_2H_5O}\;\mathrm{OC} \\ \mathrm{CO\cdot NH}\;\mathrm{H}\quad \mathrm{C_2H_5O}\;\mathrm{OC} \end{array} \longrightarrow \mathrm{NH}{<}\begin{array}{l}\mathrm{CO\cdot CO}\\ \mathrm{CO\cdot CO}\end{array}{>}\mathrm{NH}.$$

Light is thrown on the configuration of this compound by the fact that it forms a monohydrazone, mono- and di-sodium salts, and a di-silver salt; we were not able to prepare a pure mono-silver salt.

Cold sodium hydrogen carbonate acts on the substance with effervescence to form a white mono-salt; the di-salt is obtained by the use of sodium hydroxide, but the action in this case is complicated by the fact that hydrolysis is concurrent, and we could only obtain the pure salt by using the alkali in the form of the theoretical amount of sodium alkyloxide, all moisture being carefully excluded. These reactions point to the probability of the existence of one hydroxyl group in the molecule reacting directly with sodium hydrogen carbonate to form a mono-sodium salt, and to the possible presence of a second hydroxyl group by tautomeric rearrangement between the CO· and NH· groups under the influence of stronger alkali. The substance has thus probably the following constitution:



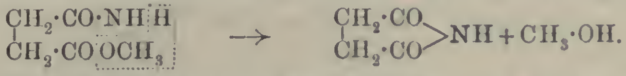
$$\mathrm{N}{\lessdot}\begin{array}{l}\mathrm{C(OH)\cdot CO}\\ \mathrm{CO{-\!-\!-}CO}\end{array}{>}\mathrm{NH}.$$

This formula shows one of the ketonic groups to be different in nature from the others, and this may account for the formation of a monohydrazone. The yield of sodium salt obtained in the preparation of the substance shows the salt to be dibasic. We purpose investigating the reduction products of this substance, the action of alkyl iodides on the sodium and silver salts, and the products of the interaction which takes place with aniline.

EXPERIMENTAL.

Succinimide from Methyl Succinamate.—0·68 gram of sodium wire (1 atom) was placed in 100 c.c. of dry benzene, and dissolved in rather more than 1·1 gram (1 mol.) of methyl alcohol by warming on the water-bath. 0·4 gram of methyl succinamate (1 mol.) was added, and the mixture heated on the water-bath for two hours and allowed to cool. Water was then added and the aqueous part separated from the benzene, which was extracted several times with water.

The benzene portion left no residue on evaporation. The aqueous solution was shaken with a little ether to remove benzene, and air was bubbled through to remove benzene and ether. The solution, which was slightly alkaline, was acidified with hydrochloric acid and evaporated on the water-bath. The crystalline residue was dried over sulphuric acid, ground, and extracted three times with alcohol quickly raised to the boiling point. The alcoholic solution gave, on evaporation, a white crystalline solid, which after recrystallisation from absolute alcohol melted at 124° (succinimide m. p. 125°). The yield was small, but the following reaction had evidently taken place to some extent:



$$\begin{array}{l} CH_2\cdot CO\cdot NH\,\vdots\, H \\ CH_2\cdot CO\,\vdots\, OCH_3 \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CO \\ CH_2\cdot CO \end{array}\!\!>NH + CH_3\cdot OH.$$

Action of Sodium Ethoxide on Ethyl Malonamate.—Ethyl malonamate was prepared (*Ber.*, 1895, **28**, 479) by the action of a slow stream of hydrochloric acid gas on a well-cooled mixture of ethyl alcohol and ethyl cyanoacetate, and subsequent decomposition by heat of the hydrochloride of iminomalonic ester which is produced. A certain amount of ammonium chloride was formed, and the pure ester was obtained by extracting the product with acetone and allowing the solution to evaporate slowly. The resulting oil crystallised readily on cooling and stirring, and the ester melted at 49—50°. Thirteen grams were obtained from 25 grams of ethyl cyanoacetate.

(a) *Sodium Ethoxide and Ethyl Malonamate in Benzene Solution.*—2·3 grams (1 atom) of sodium wire were suspended in 100 c.c. of dry benzene and dissolved in 4·6 grams of ethyl alcohol by the aid of heat. After cooling, 13·1 grams (1 mol.) of ethyl malonamate in benzene solution were added, and the whole allowed to stand overnight. The mixture was then heated on the water-bath for two hours, cooled, and the solid which had separated was filtered and dried. Yield about 16·2 grams.

In this and all other similar reactions a deep indigo-blue colour developed, which only disappeared on the addition of water.

The benzene portion was added to iced water, but no precipitation took place and the water remained neutral and colourless. The benzene left no residue on evaporation.

The solid product was white and almost completely soluble in water, from which a buff-coloured substance was precipitated by dilute hydrochloric, though not by acetic acid. The bulk was treated with water, the residue separated, and on adding dilute hydrochloric acid to the filtrate a pale brown amorphous precipitate was obtained; the product burnt without melting on platinum foil, leaving a very slight residue. The yield was 7·2 grams. This substance dissolves readily in warm methyl alcohol, from which it separates as a crystalline powder on cooling; there is some slight decomposition as the mother liquor assumes a reddish tint. It is insoluble in ether, benzene or water, but dissolves readily in aqueous sodium hydrogen carbonate with effervescence. Ammonia was evolved on heating the substance. A neutral solution gave a yellow precipitate with silver nitrate, reduction taking place on warming; salts of copper, lead, and mercury were also obtained, but barium chloride only gave a precipitate on boiling.

The crude product was crystallised from aqueous methyl alcohol.

0·1825 gave 23·2 c.c. moist nitrogen at 16° and 739 mm. N = 14·40.

$C_3H_5O_3N$ requires N = 13·58 per cent.

$2C_3H_5O_3N - H_2O$ requires N = 14·89 per cent.

Titration with baryta solution [1 c.c. = 0·00822 $Ba(OH)_2$].

0·1065 required 6 c.c. Equivalent = 185·07.

0·1016 „ 5·6 c.c. „ = 189·6.

Titration with sodium hydroxide solution (1 c.c. = 0·0040 NaOH).

0·1021 required 5·3 c.c. Equivalent = 190·8.

Mean of three results = 188·49.

$C_3H_5O_3N$ (Malonamic acid) requires equivalent = 206.

$2C_3H_5O_3N - H_2O$ requires equivalent = 188.

It has been found impossible to hydrolyse ethyl malonamate to malonamic acid by any of the usual methods. Malonic acid is the chief substance obtained together with some decomposition products.

(b) *Action of Sodium Ethoxide on Ethyl Malonamate in Absence of Benzene.*—0·72 gram of sodium (1 atom) was treated with just sufficient alcohol to convert the metal into sodium ethoxide, and while the latter was still molten 3·9 grams (1 mol.) of ethyl malonamate were added. Reaction appeared to take place immediately. The mixture was heated on the water-bath for half an hour and afterwards in a paraffin bath at 150° for one hour. After cooling it was treated with water, in which it dissolved to a yellow solution, leaving only a trace of insoluble residue. The solution was filtered and acidified with hydrochloric acid, when a buff-coloured precipitate was obtained; this was filtered, washed with cold water until free from chloride, and dried in a vacuum. Yield 0·75 gram.

The product burnt completely on platinum foil, leaving no residue. It dissolved with effervescence in cold aqueous sodium hydrogen carbonate and was reprecipitated on adding hydrochloric acid to the solution. In all its properties it resembled the substance obtained by method (*a*) in benzene solution.

The acid filtrate was neutralised with sodium carbonate solution, evaporated to a small bulk, and then allowed to stand over concentrated sulphuric acid in a vacuum. A red substance separated, which appeared to be similar to the product obtained from the methyl alcoholic solution after recrystallising the acid. This substance is being further investigated.

Action of Sodium Ethoxide on Oxamethane.

(a) *In Benzene Solution.*—3·93 grams of sodium wire (1 atom) were suspended in 100 c.c. of dry benzene and just sufficient absolute alcohol added to convert the metal completely into sodium ethoxide. Twenty grams of oxamethane (1 mol.) were then added, and the mixture was boiled for two hours on the water-bath. Some solid separated which was filtered off. The benzene gave on evaporation a small amount of unchanged oxamethane.

The solid product was treated several times with cold water, when most of it dissolved; the residue consisted of the sodium salt of tetraketopiperazine as described under method (*b*). The solution was neutralised with aqueous sodium hydrogen carbonate and concentrated on the water-bath. On adding absolute alcohol to the cold solution a voluminous white precipitate was obtained, which was filtered and dried in a vacuum. This sodium salt evolved ammonia when treated with caustic soda in the cold, thus pointing to the probability of its being sodium oxamate.

0·1993 gave 0·1251 Na_2SO_4. Na = 20·32.

0·1149 gave 12·7 c.c. moist nitrogen at 23° and 761 mm. N = 12·47.

$C_2H_2O_3NNa$ requires Na = 20·72; N = 12·61 per cent.

Thus the reaction in benzene solution yields principally sodium oxamate.

(b) *Direct Action in Absence of Benzene.*—3·9 grams of sodium (1 atom) were dissolved in just sufficient absolute alcohol to convert the metal into sodium ethoxide. After cooling, 20 grams of oxamethane (1 mol.) were added and the mixture heated in the paraffin bath. At 125—130° a violent reaction took place; the mixture became pale brown and alcohol was evolved. This was allowed to escape in order to prevent any hydrolysing action taking place. After heating at 140° for about one hour, the mass was cooled and treated several times with hot benzene in order to extract oxamethane, of which a small quantity remained unchanged. The product was then treated with cold water, in which it was only very slightly soluble, filtered, washed with water and alcohol, and dried. The weight of dry sodium salt obtained was 29 grams. (Theory for disodium tetraketopiperazine = 33·4 grams.)

It is a pale yellow powder, only sparingly soluble in cold water, and is decomposed when treated with hydrochloric acid, sodium chloride being formed, together with a substance which on analysis gave figures corresponding to tetraketopiperazine.

The latter substance burnt on platinum foil without melting and left a slight ash which gave an alkaline reaction towards litmus. It did not melt in a capillary tube, but slowly blackened above 250°.

It was insoluble in most organic solvents, but dissolved fairly readily in boiling glacial acetic acid, from which it crystallised in small, almost colourless monoclinic prisms. It dissolved with effervescence in warm aqueous sodium hydrogen carbonate, the sodium salt being precipitated.

The latter appears to be more insoluble than the free tetraketone; the potassium salt is more soluble.

For analysis the recrystallised product was heated for three hours at 110° in an air oven, in order to remove any traces of acetic acid.

0·1855 gave 0·2312 CO_2 and 0·0421 H_2O. C = 33·99; H = 2·52.
0·1819 ,, 32 c.c. moist nitrogen at 21° and 767 mm. N = 20·22.
0·1828 ,, 32·1 c.c. ,, ,, ,, 22° ,, 774 mm. N = 20·26.
$C_4H_2O_4N_2$ requires C = 33·80; H = 1·40; N = 19·71 per cent.

The numbers obtained indicate that the substance was not quite pure, but recrystallisation was difficult owing to its insolubility. It is possible that boiling with acetic acid brings about decomposition to some extent.

The substance was dissolved in a large excess of cold water, and titrated with baryta solution, using phenolphthalein as indicator (1 c.c. baryta = 0·0082 $Ba(OH)_2$).

0·1005 required 7·35 c.c. for neutralisation.
Equivalent found = 142·2. $C_4H_2O_4N_2$ requires 142.

This corresponds to the formation of a monosodium salt, but the tendency to form a disodium salt was shown by the fact that on standing the red colour disappeared and further baryta was required before it reappeared.

The point of complete neutralisation corresponding to a disodium salt cannot, however, be reached in this way owing to hydrolysis (see sodium salts).

Sodium Salts of Tetraketopiperazine.

The *mono-salt* was obtained by treating the tetraketopiperazine with excess of sodium hydrogen carbonate solution in the cold. Partial solution took place with effervescence and reprecipitation on standing.

On isolation the substance was obtained in long, white, silky needles, and proved to be free from carbonate. It dissolved in water with the exception of a small yellow residue which was in every respect like the disodium salt, and the presence of this accounts for the slightly high number obtained on analysis:

0·2130 dried at 110° gave 0·0977 Na_2SO_4. Na = 14·85.
$C_4HO_4N_2Na$ requires Na = 14·02 per cent.
$C_4O_4N_2Na_2$,, Na = 24·70 ,, ,,

The *disodium salt* cannot be prepared in a pure state by the action of aqueous sodium hydroxide on the parent substance or on the mono-salt owing to the fact that a partial hydrolysis takes place as already described. It is best prepared by the method given for the preparation of tetraketopiperazine itself, that is, by treating oxamethane with the theoretical amount of sodium ethoxide. Even in this case a certain amount of hydrolysis is caused by the necessary purification as shown by the figures obtained:

0·1936 dried at 110° gave 0·1368 Na_2SO_4. Na = 22·88.

$C_4O_4N_2Na_2$ requires Na = 24·70 per cent.
$C_4HO_4N_2Na$ „ Na = 14·02 „ „

Silver Salt.—This was obtained from the more soluble potassium salt as a voluminous white precipitate. After drying,

0·1042 gave 0·0632 Ag. Ag = 60·65.

$C_4O_4N_2Ag_2$ requires Ag = 60·67 per cent.
$C_4HO_4N_2Ag$ „ Ag = 43·37 „ „

Hydrazone.—The tetraketopiperazine was dissolved in warm acetic acid and a solution of phenylhydrazine in acetic acid was added. The liquid became yellow and was warmed on the water-bath for five minutes, when fine needles separated. The product was re-crystallised from acetic acid and a buff-coloured crystalline substance obtained, which on heating began to sinter at 250° and decomposed without melting completely below 300°.

0·1071 gave 22·4 c.c. moist nitrogen at 20° and 767·5 mm. N = 24·15.

$C_{10}H_8O_3N_4$ (monohydrazone) requires N = 24·13 per cent.
$C_{16}H_{14}O_2N_6$ (dihydrazone) requires N = 26·08 per cent.

Tetraketopiperazine dissolves sparingly in water, forming a solution which has an acid reaction; on addition of ammonium hydroxide an *ammonium* salt is precipitated which dissolves on dilution. This salt is decomposed by hydrochloric acid with the formation of the parent substance. A *mercury* salt was also obtained.

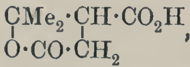
On boiling with aniline a white crystalline compound is formed which sublimes with great readiness to a voluminous white product, melting between 210—215°. It is decomposed on treatment with boiling aqueous caustic potash, aniline being evolved. This product will be further investigated.

THE ORGANIC LABORATORIES,
UNIVERSITY OF LIVERPOOL.

XVII.—*Synthesis of Terebic, Terpenylic, and Homoterpenylic Acids.*

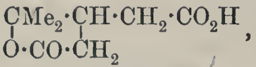
By John Lionel Simonsen
(Schunck Research Fellow in the University of Manchester).

The three acids,



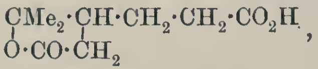
$$\begin{array}{l} CMe_2\cdot CH\cdot CO_2H \\ O\cdot CO\cdot CH_2 \end{array},$$

Terebic acid



$$\begin{array}{l} CMe_2\cdot CH\cdot CH_2\cdot CO_2H \\ O\cdot CO\cdot CH_2 \end{array},$$

Terpenylic acid



$$\begin{array}{l} CMe_2\cdot CH\cdot CH_2\cdot CH_2\cdot CO_2H \\ O\cdot CO\cdot CH_2 \end{array},$$

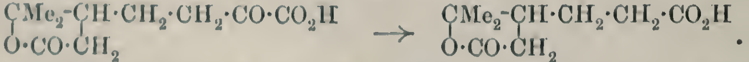
Homoterpenylic acid

are all produced by the action of oxidising agents on pinene and have always been considered of great importance, since the determination of their constitution has done much to solve the difficult problem of the constitution of pinene.

The constitution of terebic acid has been very carefully investigated by Fittig and his pupils (*Annalen*, 1876, **180**, 45; 1881, **208**, 37; 1883, **220**, 254; 1884, **226**, 365; 1899, **304**, 220), and the acid has also been obtained synthetically by several methods (*Ber.*, 1893, **26**, 2047, 2315; Trans., 1899, **75**, 531; *Compt. rend.*, 1906, **142**, 1477), perhaps the most important being that carried out by Blaise (*Compt. rend.*, 1898, **126**, 349), who obtained it by the action of acetone on ethyl bromosuccinate in the presence of the zinc–copper couple.

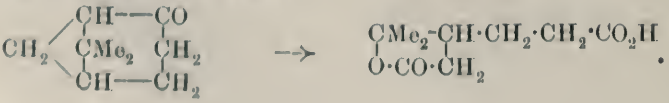
The formula given above for terpenylic acid was first suggested by Wallach (*Annalen*, 1890, **259**, 322) and subsequently shown to be correct by the careful investigations of Fittig (*Annalen*, 1896, **288**, 176), Mahla and Tiemann (*Ber.*, 1896, **29**, 928), and Schryver (Trans., 1893, **63**, 1338). Lawrence (Trans., 1899, **75**, 531) succeeded in obtaining this acid synthetically by oxidising β-*iso*propylglutaric acid by means of chromic acid solution, and thus there can be no doubt as to its constitution.

Homoterpenylic acid was first obtained by Baeyer (*Ber.*, 1896, **29**, 1919) by the oxidation of homoterpenoylformic acid (an oxidation product of pinene) with nitric acid or lead oxide.



$$\begin{array}{l} CMe_2\text{-}CH\cdot CH_2\cdot CH_2\cdot CO\cdot CO_2H \\ O\cdot CO\cdot CH_2 \end{array} \longrightarrow \begin{array}{l} CMe_2\text{-}CH\cdot CH_2\cdot CH_2\cdot CO_2H \\ O\cdot CO\cdot CH_2 \end{array}.$$

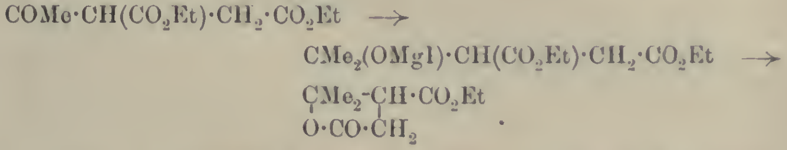
In conjunction with Villiger (*Ber.*, 1896, **29**, 1923) he also obtained it by the oxidation of nopinone:



Its constitution was deduced by Baeyer (*Ber.*, 1896, **29**, 2775) from the fact that on oxidation it yielded a mixture of terebic and terpenylic acids.

In considering the formulæ of these acids it seemed probable that a convenient method of synthesis would be to act on the corresponding keto-ester with magnesium methyl iodide, especially since it is known that in such cases the keto-group reacts with the reagent before the carbethoxy-group is attacked (compare W. H. Perkin, jun., Trans., 1904, **85**, 654). It has already been noticed (Grignard, *Compt. rend.*, 1902, **135**, 629; Jones and Tattersall, Trans., 1904, **85**, 1691) that keto-esters containing the keto-group in the γ-position react with magnesium methyl iodide with the direct formation of lactones.

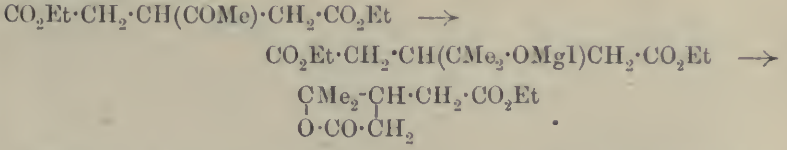
This process was first applied to ethyl acetosuccinate, which, when treated with magnesium methyl iodide, is directly converted into ethyl terebate:



$$\mathrm{COMe\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et} \longrightarrow \mathrm{CMe_2(OMgI)\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et} \longrightarrow \begin{array}{l}\mathrm{CMe_2{-}CH\cdot CO_2Et}\\ \mathrm{O\cdot CO\cdot CH_2}\end{array}.$$

The yield of this ester is good, and, since simply boiling with hydrochloric acid converts it readily into terebic acid, it is probable that this synthesis constitutes the most convenient method for the preparation of this acid.

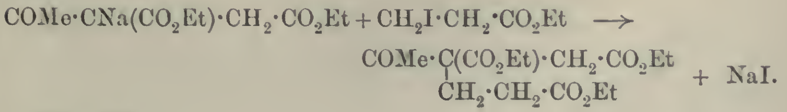
Under similar conditions ethyl β-acetylglutarate is found to react readily with magnesium methyl iodide with formation of ethyl terpenylate:



$$\mathrm{CO_2Et\cdot CH_2\cdot CH(COMe)\cdot CH_2\cdot CO_2Et} \longrightarrow \mathrm{CO_2Et\cdot CH_2\cdot CH(CMe_2\cdot OMgI)CH_2\cdot CO_2Et} \longrightarrow \begin{array}{l}\mathrm{CMe_2{-}CH\cdot CH_2\cdot CO_2Et}\\ \mathrm{O\cdot CO\cdot CH_2}\end{array}.$$

This ester is again obtained in a good yield and, when digested with hydrochloric acid, is at once converted into terpenylic acid.

In order to synthesise homoterpenylic acid it was necessary in the first place to prepare β-acetyladipic acid. This was readily done by treating the sodium compound of ethyl acetosuccinate with ethyl β-iodopropionate, when ethyl β-acetylbutane-$\alpha\beta\delta$-tricarboxylate is formed:



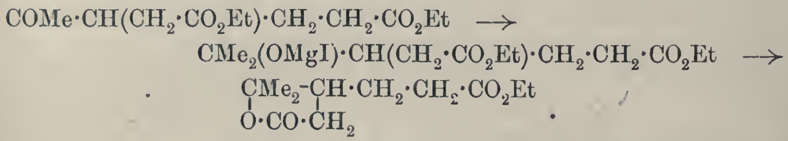
$$\mathrm{COMe\cdot CNa(CO_2Et)\cdot CH_2\cdot CO_2Et + CH_2I\cdot CH_2\cdot CO_2Et} \longrightarrow \begin{array}{l}\mathrm{COMe\cdot C(CO_2Et)\cdot CH_2\cdot CO_2Et}\\ \qquad\quad\mathrm{CH_2\cdot CH_2\cdot CO_2Et}\end{array} + \mathrm{NaI}.$$

When this ester is digested with hydrochloric acid it is hydrolysed, carbon dioxide is eliminated, and β-acetyladipic acid,

$$\mathrm{COMe\cdot CH(CH_2\cdot CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H},$$

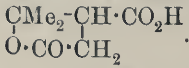
a crystalline substance melting at 102°, is produced.

The ester of this acid reacts readily with magnesium methyl iodide with formation of ethyl homoterpenylate:



$$\mathrm{COMe\cdot CH(CH_2\cdot CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et} \longrightarrow \mathrm{CMe_2(OMgI)\cdot CH(CH_2\cdot CO_2Et)\cdot CH_2\cdot CH_2\cdot CO_2Et} \longrightarrow \begin{array}{l}\mathrm{CMe_2{-}CH\cdot CH_2\cdot CH_2\cdot CO_2Et} \\ \mathrm{O\cdot CO\cdot CH_2}\end{array}$$

This ester on hydrolysis yielded homoterpenylic acid which melted at 100—101° and had all the properties ascribed to it by Baeyer.

Synthesis of Terebic Acid,  $\begin{array}{l}\mathrm{CMe_2{-}CH\cdot CO_2H} \\ \mathrm{O\cdot CO\cdot CH_2}\end{array}$.—In preparing this acid, ethyl acetosuccinate (21 grams), mixed with about four times its volume of dry ether, was slowly added to a well-cooled ethereal solution of magnesium methyl iodide (prepared from 21 grams of methyl iodide and 4 grams of magnesium). The reaction is extremely vigorous and the white magnesium compound soon separates. After standing overnight the magnesium compound was carefully decomposed by the slow addition of water and dilute hydrochloric acid; the ethereal layer was then separated and the acid solution extracted twice with small quantities of ether. The mixed ethereal extracts were washed with a little sodium hydrogen sulphite solution, to remove iodine, and afterwards dried and evaporated.

The residual yellow oil was fractionated under reduced pressure (18 mm.), when it all passed over at 140—150°, and, on refractionating, almost the whole quantity distilled constantly at 145—147° (15 mm.), and evidently contained some unchanged ethyl acetosuccinate, since it still gave a violet coloration with ferric chloride.

In order to obtain terebic acid the crude product (17 grams) was hydrolysed by boiling in a reflux apparatus with concentrated hydrochloric acid (50 c.c.). Owing to the presence of the ethyl acetosuccinate some carbon dioxide was evolved at first and after heating for eight hours the oil had completely dissolved. The hydrochloric acid was evaporated, when a semi-solid brown mass remained, which was dissolved in hot water and boiled for a few minutes with animal charcoal.

The solution was filtered and concentrated, when, on cooling, colourless needles were deposited. After collecting and recrystallising from water, the following results, agreeing with those required by terebic acid were obtained on analysis:

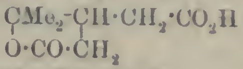
0·1524 gave 0·2978 $\mathrm{CO_2}$ and 0·0850 $\mathrm{H_2O}$. C = 53·2; H = 6·2.

$\mathrm{C_7H_{10}O_4}$ requires C = 53·2; H = 6·3 per cent.

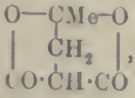
The acid melted at 174°, which is the melting point given by Fittig and Melck (*Annalen*, 1876, **180**, 45) to terebic acid. The characteristic barium salt of the diaterebic acid was also prepared by boiling the solution of terebic acid with excess of baryta, removing the excess with carbon dioxide, and precipitating the barium diaterebate with alcohol.

0·4589 gave 0·2940 $BaSO_4$. Ba = 37·6.

$C_7H_{10}O_5Ba + 3H_2O$ requires Ba = 37·5 per cent.

Terpenylic Acid, 

$$\begin{matrix} CMe_2\text{-}CH\cdot CH_2\cdot CO_2H \\ O\cdot CO\cdot CH_2 \end{matrix}$$

.—Ethyl β-acetylglutarate, $CO_2Et\cdot CH_2\cdot CH(COMe)\cdot CH_2\cdot CO_2Et$, was found to be most readily obtained from the dilactone of β-acetylglutaric acid, 

$$\begin{matrix} O\text{—}CMe\text{—}O \\ CH_2 \\ CO\cdot CH\cdot CO \end{matrix}$$

, by the method described by Fittig (*Annalen*, 1900, **314**, 21), who obtained this dilactone from the sodium salt of tricarballylic acid by heating with acetic anhydride.

In preparing terpenylic acid, ethyl β-acetylglutarate (20 grams), dissolved in about four times its volume of dry ether, was slowly added to a well-cooled ethereal solution of magnesium methyl iodide (prepared from 5 grams of magnesium and 25 grams of methyl iodide). After standing overnight the magnesium compound was cautiously decomposed with water and dilute hydrochloric acid; the ethereal layer was then separated and the acid solution extracted twice with a little ether. The combined ethereal extracts were washed with a little sodium hydrogen sulphite solution, to remove iodine, and afterwards dried and evaporated. The oil thus obtained when fractioned under reduced pressure (15 mm.) passed over almost completely between 140—175°, a small quantity only of a substance of higher boiling point remaining in the distilling flask.

On refractionating, the distillate was readily separated into two portions boiling at 155—161° and 169—171° (15 mm.), and the high boiling fraction, when cooled in a freezing mixture, crystallised.

The mass was left in contact with porous porcelain until free from oil and then purified by recrystallisation from ether, when colourless crystals were obtained which melted at 37°; this is the melting point given to ethyl terpenylate by Fittig and Levy (*Annalen*, 1899, **256**, 112), and the identity was confirmed by analysis and subsequent hydrolysis.

0·1599 gave 0·3506 CO_2 and 0·1122 H_2O. C = 59·8; H = 7·8.

$C_{10}H_{16}O_4$ requires C = 60·0; H = 8·0 per cent.

The ethyl terpenylate (6 grams) was hydrolysed by boiling with concentrated hydrochloric acid (50 c.c.) when, after eight hours, the oil had completely dissolved. The hydrochloric acid was removed by evaporation on the water-bath and the residual crystalline mass purified by recrystallising from water with the aid of animal charcoal. In this way colourless prisms were obtained which showed the characteristic properties of terpenylic acid; namely, when left in the air until dry, the melting point was 56°, but after exposure over sulphuric acid for some days the melting point was found to be 89° (compare Lawrence, *loc. cit.*).

The acid melting at 89° gave the following results on analysis:

0·1611 gave 0·3301 CO_2 and 0·1006 H_2O. C = 55·9; H = 6·9.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

β-Acetyladipic Acid, $COMe·CH(CH_2·CO_2H)·CH_2·CH_2·CO_2H$.

Preparation of ethyl β-acetylbutane-αβδ-tricarboxylate,
$CO_2Et·CH_2·CH_2·CAc(CO_2Et)·CH_2·CO_2Et$.

This substance, which has not previously been described, was readily obtained as follows. Sodium (5·7 grams) was dissolved in alcohol (100 c.c.), and, after cooling, ethyl acetosuccinate (54 grams) was added. The sodium compound was then mixed with ethyl β-iodopropionate (60 grams) in small quantities at a time, any rise of temperature being carefully avoided by cooling with water. After standing overnight the mixture was heated on the water-bath for half an hour and the liquid, which should be quite neutral, was cooled and diluted with water. A heavy oil separated which was extracted three times with ether; the ethereal solution was well washed with water to remove alcohol, dried, and evaporated.

The oil thus obtained was fractionated under reduced pressure (16 mm.), when almost the whole quantity (70 grams) passed over between 195—205°, and after refractionation at 200—201° (14 mm.).

0·1643 gave 0·3418 CO_2 and 0·1120 H_2O. C = 56·7; H = 7·6.

$C_{15}H_{24}O_7$ requires C = 56·9; H = 7·6 per cent.

Ethyl β-acetylbutane-αβδ-tricarboxylate is a viscid colourless oil having a pleasant ethereal odour. It gives no coloration with ferric chloride.

In order to prepare β-acetyladipic acid this ester (70 grams) was hydrolysed by boiling with concentrated hydrochloric acid (140 c.c.) in a flask provided with a reflux condenser. At first there was much frothing owing to the evolution of carbon dioxide, and after eight hours water (100 c.c.) was added and the solution boiled for a further period of eight hours. The hydrochloric acid was then removed on the water-bath, when a very viscous yellow syrup was obtained which, on vigorous rubbing, solidified to a crystalline mass.

The β-acetyladipic acid (40 grams) was crystallised from dry ether, from which it separated in plates, melting at 102°. That this was the acid, and not either the dilactone or the semilactone of β-acetyladipic acid, as might be expected from analogy with β-acetylglutaric acid, is shown by the following analysis:

0·1423 gave 0·2653 CO_2 and 0·0824 H_2O. C = 50·8; H = 6·4.
$C_8H_{12}O_5$ requires C = 51·1; H = 6·4 per cent.

β-Acetyladipic acid is readily soluble in water, alcohol, acetone, acetic acid, formic acid, or ethyl acetate in the cold; sparingly so in ether, benzene, or chloroform, even on boiling; and almost insoluble in light petroleum.

The basicity of the acid was determined in the first place by titration with standard aqueous caustic potash.

0·1349 neutralised 0·0793 KOH, whereas this amount of a dibasic acid, $C_8H_{12}O_5$, should neutralise 0·0797 KOH.

The *silver salt* of β-acetyladipic acid was prepared by adding silver nitrate to a slightly alkaline solution of the ammonium salt, when it separated as a flocculent precipitate readily soluble in hot water from which it was crystallised.

0·1117 gave 0·0598 Ag. Ag = 53·5.
$C_8H_{10}O_5Ag_2$ requires Ag = 53·7 per cent.

β-Acetyladipic acid semicarbazone.—When an aqueous solution of β-acetyladipic acid was mixed with semicarbazide, hydrochloride, and sodium acetate nothing separated, but after some time the semicarbazone was slowly deposited in warty masses. After crystallising from hot water in which the substance is readily soluble, the following results were obtained:

0·2071 gave 0·3109 CO_2 and 0·1175 H_2O. C = 40·9; H = 6·3.
0·1654 ,, 22·3 c.c. nitrogen at 19° and 767 mm. N = 15·7.
$C_9H_{15}O_5N_3,H_2O$ requires C = 41·1; H = 6·5; N = 15·9 per cent.

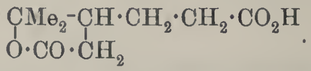
This substance, which melts at 89—90° and is sparingly soluble in cold water, is probably the semicarbazone of β-acetyladipic acid, crystallising with one molecule of water of crystallisation. That it is not simply the semicarbazide salt of the acid is shown by the fact that it dissolves instantly in sodium hydrogen carbonate solution.

Ethyl β-acetyladipate.—In order to prepare this ester β-acetyladipic acid (35 grams) was dissolved in a mixture of alcohol (175 c.c.) and sulphuric acid (17 c.c.) and boiled for two days on the water-bath. After cooling, the mixture was poured into water, when a heavy oil separated which was extracted twice with ether. The ethereal extract was well washed with dilute aqueous sodium carbonate, dried, evaporated, and the yellow oil fractioned under reduced pressure (18 mm.), when it distilled constantly at 179°.

0·1501 gave 0·3237 CO_2 and 0·1108 H_2O. C = 58·8; H = 8·2.
$C_{12}H_{20}O_5$ requires C = 59·0; H = 8·2 per cent.

Ethyl β-acetyladipate is a colourless oil with a slight but rather unpleasant odour. It is insoluble in water but readily miscible with most organic solvents.

Preparation of Homoterpenylic Acid,



$$\begin{array}{l} \text{CMe}_2\text{-CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \\ \text{O}\cdot\text{CO}\cdot\text{CH}_2 \end{array}.$$

In the preparation of homoterpenylic ester, β-acetyladipic ester (29 grams), dissolved in about four times its volume of dry ether, was slowly added to a well-cooled ethereal solution of magnesium methyl iodide (prepared from 4 grams of magnesium and 25 grams of methyl iodide). After standing overnight the magnesium compound was cautiously decomposed with water and dilute hydrochloric acid, the ethereal layer separated, and the acid solution extracted twice with small quantities of ether. The combined ethereal extract was washed with sodium hydrogen sulphite solution, dried and evaporated, when a viscid oil was obtained which after several fractionations distilled constantly at 186° (18 mm.).

0·1329 gave 0·3140 CO_2 and 0·1041 H_2O. C = 61·5 ; H = 8·3.

$C_{11}H_{18}O_4$ requires C = 61·7 ; H = 8·4 per cent.

Ethyl homoterpenylate, which has not been previously described, is a viscous colourless oil with a pleasant ethereal odour. It does not solidify even when cooled to − 15°.

Ethyl homoterpenylate was readily hydrolysed by digestion with concentrated hydrochloric acid, and, after evaporating, a viscid colourless syrup was obtained which solidified on cooling. The substance was purified by crystallising from hot water with the aid of animal charcoal and separated in colourless plates melting at 100—101°. Baeyer (*Ber.*, 1896, **29**, 1919) gives the melting point as 98—101° when crystallised from water and as 100—102·5° when ether is the solvent.

0·1866 gave 0·3950 CO_2 and 0·1266 H_2O. C = 57·7 ; H = 7·5.

$C_9H_{14}O_4$ requires C = 58·0 ; H = 7·5 per cent.

By titration with standard aqueous caustic potash in the cold, the acid was shown to be monobasic.

0·1650 neutralised 0·04963 KOH, whereas this amount of a monobasic acid of the formula $C_9H_{14}O_4$ should neutralise 0·04967 KOH.

There can, therefore, be no doubt that the synthetical acid is identical with the homoterpenylic acid obtained by the oxidation of pinene.

In conclusion I wish to thank Professor W. H. Perkin for the great interest he has shown in this research and also for much valuable advice and assistance.

THE SCHUNCK LABORATORY,
THE UNIVERSITY, MANCHESTER.

XVIII.—*Preparation of Chromyl Dichloride.*

By HERBERT DRAKE LAW and FREDERICK MOLLWO PERKIN.

THE method usually given for the preparation of chromyl dichloride is to act on a mixture of potassium dichromate and sodium chloride with concentrated sulphuric acid. Étard (*Ann. Chim. Phys.*, 1881, [v], **22**, 218) used fuming sulphuric acid and noticed that chlorine was always given off during the reaction, but he succeeded in obtaining a yield of 70 per cent. of chromyl dichloride. As a matter of fact, a certain amount of reduction of the chromyl chloride with the excess of hydrochloric acid, liberated in the reaction, always takes place, even when ordinary strong sulphuric acid is used. The objection to the above method of preparation is the extreme frothing and fuming which occurs. In order to lessen the frothing, it is generally recommended to fuse sodium chloride and potassium dichromate together in equivalent proportions, and then to break up the fused product into small pieces. Even when this is done the operation requires constant attention, and it is very difficult to distil the chromyl chloride owing to the frothing.

Moissan (*Compt. rend.*, 1884, **98**, 582) prepared it by passing dry hydrogen chloride over chromic anhydride, but even by this method a certain amount of reduction takes place, a green substance being left behind at the end of the reaction.

We tried several methods for preparing the product, for example, that of passing dry hydrogen chloride into chromic anhydride suspended in concentrated sulphuric acid, the mixture being cooled by running water. This method gave practically theoretical results, but the process was tedious owing to a tendency of the chromic anhydride to cake in the sulphuric acid, when it is only slowly acted on by the hydrochloric acid. We found the most satisfactory method was to dissolve chromic anhydride in concentrated hydrochloric acid and then to add an excess of strong sulphuric acid.

Chromic anhydride dissolves with the greatest ease in concentrated hydrochloric acid, forming a brownish-red solution. On adding concentrated sulphuric acid to this solution and cooling, chromyl dichloride separates, and, being denser than the hydrochloric-sulphuric acid solution, sinks to the bottom, and is readily isolated by means of a tap funnel. We find that if large quantities of chromic anhydride are acted on at one time the reaction does not proceed as smoothly as when smaller quantities are used, owing to the difficulty of cooling the mixture and thus keeping the reaction under control. When the reaction becomes too vigorous, and consequently heating results, the yield is much smaller, owing to reduction of the chromyl dichloride. The best results were obtained by proceeding as follows.

Fifty grams of chromic anhydride are dissolved in rather more than the calculated quantity of concentrated hydrochloric acid (170 c.c.) in a $1\frac{1}{2}$ litre flask and then 100 c.c. of concentrated sulphuric acid added in quantities of about 20 c.c. at one time, the mixture being cooled between each addition. The sulphuric acid should be poured into the middle of the solution and not down the sides of the flask, as it then mixes better and very little fuming takes place. The whole of the sulphuric acid may be added in the course of about two minutes.

In order to prepare larger quantities, about six flasks are taken, and into each flask 50 grams of chromic anhydride are placed and then the requisite quantity of hydrochloric acid. The chromic anhydride immediately dissolves. Sulphuric acid, 100 c.c., is then added to each flask, cooling between the additions of the acid, and when the reaction in the six flasks is complete, the contents are poured into a large separating funnel and allowed to stand for twenty minutes. At the end of this time the whole of the chromyl dichloride will have separated as an under layer, and is then drawn off from the specifically lighter layer of sulphuric and hydrochloric acids. Proceeding in this manner, there is no difficulty in preparing a kilogram or more in one hour.

Dry air is now aspirated through the chromyl dichloride for about an hour in order to remove any dissolved hydrochloric acid. It may then be distilled, when it will be found to boil constantly at 115—116°. For most purposes, however, it is sufficiently pure without this operation.

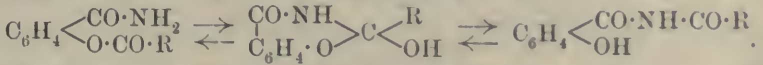
It is often stated that chromyl dichloride does not keep well. Our own experience is that, provided it is freed from hydrochloric acid by aspirating air through it and is then distilled to remove any sulphuric acid, it may be preserved for a long time. It is, however, essential to have the bottles well stoppered to exclude moisture, as, owing to absorption of the latter, the stoppers often become fixed. In using a burette or separating funnel the taps should never be lubricated with vaseline or oil, because of the vigorous action of the chromyl dichloride on hydrocarbons.

Chemical Laboratory,
Borough Polytechnic Institute,
London, S.E.

XIX.—*Benzoyl Derivatives of* N-*Methylsalicylamide.*

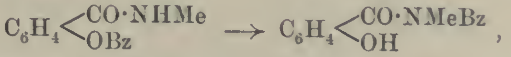
By JAMES McCONNAN and MORRIS EDGAR MARPLES.

IT has been shown (Titherley and Hicks, Trans., 1905, **87**, 1207 and McConnan and Titherley, Trans., 1906, **89**, 1318) that both *O*-acyl and *N*-acyl derivatives of salicylamide are unstable substances in the sense that they show a tendency to rearrange, and, under suitable conditions, can be converted into each other; and the view has been expressed that these changes take place through an intermediate cyclic metoxazone form, according to the scheme:



$$C_6H_4<\begin{matrix}CO\cdot NH_2\\O\cdot CO\cdot R\end{matrix} \rightleftarrows \begin{matrix}CO\cdot NH\\|\\C_6H_4\cdot O\end{matrix}>C<\begin{matrix}R\\OH\end{matrix} \rightleftarrows C_6H_4<\begin{matrix}CO\cdot NH\cdot CO\cdot R\\OH\end{matrix}.$$

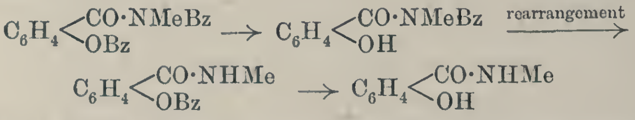
The benzoyl derivatives of *N*-methylsalicylamide have been investigated with the object of throwing further light on this interesting change. *O*-Benzoyl-*N*-methylsalicylamide is easily obtained by pyridine-benzoylation of *N*-methylsalicylamide. In its solubilities and its decomposition by cold sulphuric acid to benzoic acid and *N*-methylsalicylamide it resembles *O*-benzoylsalicylamide; it behaves abnormally, however, in all those reactions by which *O*-benzoyl salicylamide is rearranged to Gerhardt's *N*-benzoylsalicylamide. The latter rearrangement takes place, for instance, when *O*-benzoylsalicylamide is melted, when it is boiled with water, on leaving it to stand in pyridine solution for fifteen days, or on treatment with aqueous alkali. Under the first three conditions *O*-benzoyl-*N*-methylsalicylamide is not affected, but on treatment with alkali it dissolves slowly with development of a yellow colour. Whilst in the case of *O*-benzoylsalicylamide the yellow colour, due to the formation of the stable sodium derivative of *N*-benzoylsalicylamide, is persistent, with *O*-benzoyl-*N*-methylsalicylamide the colour is transient and disappears in from thirty seconds to two minutes, according to the conditions of the experiment. There can be no doubt that similar rearrangement occurs, forming the sodium derivative of *N*-benzoyl-*N*-methylsalicylamide:



$$C_6H_4<\begin{matrix}CO\cdot NHMe\\OBz\end{matrix} \longrightarrow C_6H_4<\begin{matrix}CO\cdot NMeBz\\OH\end{matrix},$$

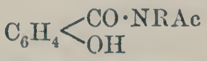
but the latter is almost instantly hydrolysed to benzoic acid and *N*-methylsalicylamide; this assumption is necessary, both by analogy with the simpler case mentioned, and from the fact that *N*-methylsalicylamide yields a colourless solution in alkalis. Numerous attempts were made to isolate *N*-benzoyl-*N*-methylsalicylamide from the yellow solution, using *O*-benzoyl-*N*-methylsalicylamide, both solid and in alcoholic solution, and varying the nature and strength of the alkaline reagent, but in all cases hydrolysis appeared to be practically instantaneous, and addition of dilute acid to the yellow solution produced at most a precipitate of unchanged *O*-benzoyl-*N*-methylsalicylamide.

The extreme instability of *N*-benzoyl-*N*-methylsalicylamide is confirmed by the study of *O*-*N*-dibenzoyl-*N*-methylsalicylamide, obtained by pyridine benzoylation of *O*-benzoyl-*N*-methylsalicylamide. Were its behaviour normal it should be decomposed by cold concentrated sulphuric acid into benzoic acid and *N*-benzoyl-*N*-methylsalicylamide (compare *O*-*N*-dibenzoylsalicylamide, McConnan and Titherley, Trans., 1906, **89**, 1327), since it has been found in general that this reagent eliminates *O*-acyl groups, but leaves *N*-acyl derivatives intact. *O*-*N*-Dibenzoyl-*N*-methylsalicylamide dissolves in sulphuric acid and is decomposed ultimately into benzoic acid and *N*-methylsalicylamide, but if a relatively small quantity of acid is used *O*-benzoyl-*N*-methylsalicylamide can be isolated as an intermediate product. This behaviour is analogous to that of tribenzoylsalicylamide, and is represented by the scheme:



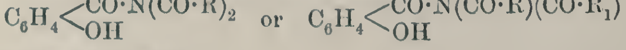
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NMeBz}{OBz} \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NMeBz}{OH} \xrightarrow{\text{rearrangement}}$$
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NHMe}{OBz} \longrightarrow C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NHMe}{OH}$$

Since *N*-*N*-dimethylsalicylamide is a stable substance melting at 164°, it appears that although derivatives of the general formula $C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NR_2}{OH}$ are stable, substances of the type



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NRAc}{OH}$$

are too unstable to permit of isolation. This observation is of considerable interest, since McConnan and Titherley have already shown (*loc. cit.*) that *N*-*N*-diacyl salicylamides,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot N(CO\cdot R)_2}{OH} \quad \text{or} \quad C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot N(CO\cdot R)(CO\cdot R_1)}{OH}$$

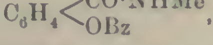
are too unstable to exist.

Experimental.

N-*Methylsalicylamide*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NH\cdot Me}{OH}$.—This compound, which has not been hitherto described, was prepared by the action of aqueous methylamine on salol. 214 grams of salol and 200 grams of 33 per cent. methylamine solution were allowed to stand for twelve hours with occasional shaking; the mixture became warm, and the reaction was completed by warming until all was in solution. The excess of methylamine was distilled off, the residue acidified by dilute hydrochloric acid, and the phenol distilled in steam; the solution was filtered hot, and deposited *N*-methylsalicylamide on cooling; a further crop of crystals was obtained by concentrating the mother liquor. The product was recrystallised from dilute alcohol; yield: 95 per cent. of theory:

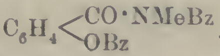
0·1867 gave 14·8 c.c. nitrogen at 19° and 772 mm. N = 9·26.
$C_8H_9O_2N$ requires N = 9·27 per cent.

N-*Methylsalicylamide* melts at 89°; it is readily soluble in alcohol, ether, benzene, or chloroform, and crystallises from dilute alcohol in colourless plates; its behaviour with alkaline reagents and with ferric chloride is in every respect analogous to that of salicylamide.

O-*Benzoyl*-N-*methylsalicylamide*,  $C_6H_4<^{CO\cdot NHMe}_{OBz}$, was prepared by adding 14 grams of benzoyl chloride to a solution of 15 grams of *N*-methylsalicylamide in 45 grams of pyridine at −15°; the product was isolated in the usual way and recrystallised from benzene.

0·1785 gave 9·0 c.c. nitrogen at 21° and 745 mm. N = 5·63.
$C_{15}H_{13}O_3N$ requires N = 5·49 per cent.

O-*Benzoyl*-N-*methylsalicylamide* melts at 122°; it is readily soluble in cold alcohol or chloroform, sparingly so in ether; it crystallises from benzene in transparent, prismatic needles. On stirring with aqueous alkali it dissolves slowly, with a transient yellow colour, being almost instantly hydrolysed to benzoic acid and *N*-methylsalicylamide; it is similarly decomposed by cold concentrated sulphuric acid. Ethyl benzoate is obtained as a decomposition product when an alcoholic solution of *O*-benzoyl-*N*-methylsalicylamide is treated with alkali; with sodium ethoxide or aqueous sodium hydroxide the decomposition was complete in thirty to sixty seconds (measured by the disappearance of the yellow colour), but with alcoholic ammonia no colour change was observed, and the decomposition required several hours.

O-N-*Dibenzoyl*-N-*methylsalicylamide*,  $C_6H_4<^{CO\cdot NMeBz}_{OBz}$.—2·8 Grams of benzoyl chloride were added to a solution of 5 grams of *O*-benzoyl-*N*-methylsalicylamide in 15 grams of pyridine; after standing twelve hours the mass was stirred with absolute ether, the ethereal solution was decanted from the pyridine hydrochloride, washed with dilute sulphuric acid, and dried with sodium sulphate.

O-N-*Dibenzoyl*-N-*methylsalicylamide* separated on adding light petroleum, and was crystallised from a mixture of ether and light petroleum, from which it was obtained in large hexagonal prisms.

0·1754 gave 5·9 c.c. nitrogen at 19° and 772 mm. N = 3·93.
$C_{22}H_{17}O_4N$ requires N = 3·90 per cent.

Dibenzoyl-*N*-methylsalicylamide melts at 85°; it is readily soluble in alcohol, ether, or chloroform, moderately so in benzene, and very sparingly so in light petroleum. It is insoluble in cold aqueous caustic soda, but on boiling it is hydrolysed slowly to *N*-methylsalicylamide and benzoic acid. The same decomposition products were obtained by dissolving it in excess of cold concentrated sulphuric acid and allowing to stand for four days, whilst with a smaller quantity of sulphuric acid and only four hours' action *O*-benzoyl-*N*-methylsalicylamide was obtained as decomposition product.

ORGANIC LABORATORY,
UNIVERSITY OF LIVERPOOL.

XX.—*Disalicylamide.*

By JAMES McCONNAN.

DISALICYLAMIDE ($HO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}OH$) was first obtained by Schulerud (*J. pr. Chem.*, 1880, [ii], 22, 289) by the action of hydrogen chloride on heated salicylamide.

Subsequently G. Cohn (*J. pr. Chem.*, 1900, [ii], 61, 552) found that disalicylamide is formed when salol and salicylamide are heated together at 215—220°; at the same time he appears to have obtained a second compound which was formulated as *O*-salicylsalicylamide, $C_6H_4(CO{\cdot}NH_2){\cdot}O{\cdot}CO{\cdot}C_6H_4{\cdot}OH$, the properties of which were, however, practically identical with those of disalicylamide (*Patentschrift*, No. 111,656).

These two compounds are recorded in Beilstein's Handbuch (*Ergänzungsband II.*, 892, 893), but the author, from previous work on acyl derivatives of salicylamide (Trans., 1906, **89**, 1318), was led to doubt Cohn's conclusions as to the supposed *O*-salicylsalicylamide. The properties assigned to the latter by Cohn were inconsistent with the *O*-salicyl formula, as was also its mode of formation from salol and salicylamide, inasmuch as ammonia is evolved in the reaction; it is now known that *O*-acyl derivatives of salicylamide are instantly rearranged to the corresponding *N*-acyl derivatives by ammonia.

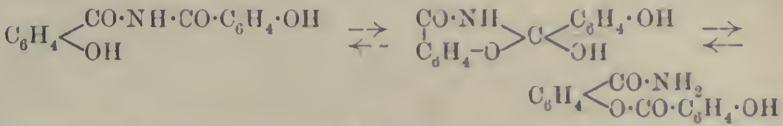
The reaction between salol and salicylamide has been repeated with the object of investigating this point, and it has been proved that *O*-salicylsalicylamide is not formed. Two compounds are produced, namely:

(1) Disalicylamide: $HO{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}OH$, m. p. 203°.

(2) Polysalicylnitrile, m. p. 297° (Limpricht, *Annalen*, 1856, **98**, 261, &c.).

The proportions of each vary, and the amount of polysalicylnitrile formed increases rapidly with the proportion of salicylamide used.

O-Salicylsalicylamide has been obtained, however, by the rearrangement of disalicylamide by boiling with glacial acetic acid, the change taking place, according to the author's view, through an intermediate cyclic form :

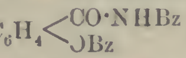


$$C_6H_4{<}\begin{matrix}CO\cdot NH\cdot CO\cdot C_6H_4\cdot OH\\ OH\end{matrix} \rightleftarrows \begin{matrix}CO\cdot NH\\ |\\ C_6H_4-O\end{matrix}{>}C{<}\begin{matrix}C_6H_4\cdot OH\\ OH\end{matrix} \rightleftarrows C_6H_4{<}\begin{matrix}CO\cdot NH_2\\ O\cdot CO\cdot C_6H_4\cdot OH\end{matrix}$$

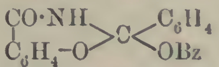
(compare rearrangement of *N*-benzoylsalicylamide, McConnan and Titherley, Trans., 1906, **89**, 1321).

O-Salicylsalicylamide undergoes the reverse change into disalicylamide on melting, on boiling with water, on standing in pyridine solution, or on treatment with alkaline reagents; the two compounds are, in fact, in every respect analogous to the two benzoyl and the two acetyl salicylamides already described (*loc. cit.*, and Titherley and Hicks, Trans., 1905, **87**, 1207).

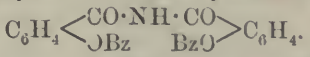
The study of disalicylamide has led to the detection of an error in the recent work on acyl derivatives of salicylamide (McConnan and Titherley, Trans., 1906, **89**, 1326); it was stated that the action of benzoyl chloride on a pyridine solution of Gerhardt's benzoyl salicylamide at −15° led to the formation of two compounds :

(1) *O*-*N*-Dibenzoylsalicylamide :  $C_6H_4{<}\begin{matrix}CO\cdot NHBz\\ OBz\end{matrix}$ (m. p. 128°).

(2) 2 : 2-Phenyl-*O*-benzoylhydroxybenzometoxazone :



$$\begin{matrix}CO\cdot NH\\ |\\ C_6H_4-O\end{matrix}{>}C{<}\begin{matrix}C_6H_4\\ OBz\end{matrix}\ \text{(m. p. 160°).}$$

All subsequent attempts to prepare the second compound in the same way failed, and it has been shown that the formation of the derivative melting at 160° was due to the unsuspected presence of disalicylamide as impurity in the benzoylsalicylamide used.* It has been found that the compound melting at 160° is easily obtained by pyridine benzoylation of disalicylamide, and that it is dibenzoyldisalicylamide :  $C_6H_4{<}\begin{matrix}CO\cdot NH\cdot CO\\ OBz\quad\ \ BzO\end{matrix}{>}C_6H_4$.

The view taken by McConnan and Titherley of the tautomeric character of Gerhardt's benzoylsalicylamide is thus deprived of one point of evidence previously adduced in its support; this view, however, has since been confirmed by new experimental evidence to be published shortly.

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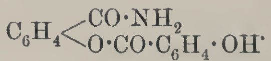
* The conditions for the production of disalicylamide are present in Gerhardt's method of preparing benzoylsalicylamide, since the method involves heating salicylamide in presence of hydrochloric acid.

EXPERIMENTAL.

O-Salicylsalicylamide,



$$C_6H_4{<}\begin{matrix}CO\cdot NH_2\\ O\cdot CO\cdot C_6H_4\cdot OH\end{matrix}$$

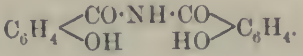
42·8 Grams of salol (1 mol.) were heated with 41·1 grams of salicylamide ($1\frac{1}{2}$ mols.) for two hours at 220°, the phenol formed by the reaction being allowed to distil off. The product was poured into 100 c.c. of alcohol, and the resulting yellow precipitate, consisting of a mixture of disalicylamide and polysalicylnitrile, was separated. The mixture was boiled for three hours with 300 c.c. of glacial acetic acid, when the disalicylamide completely dissolved, being at the same time partly rearranged to *O*-salicylsalicylamide. The insoluble polynitrile was filtered from the hot solution and washed with acetic acid and water; it weighed 4 grams and melted at 297°.

The hot acetic acid solution, on cooling and diluting with water, deposited 20 grams of a mixture of disalicylamide and *O*-salicylsalicylamide; these were separated from the dry mixture by extracting with boiling benzene, in which disalicylamide is insoluble. *O*-Salicylsalicylamide crystallised in a pure state from the hot benzene filtrate; it was filtered and washed with light petroleum.

0·2441 gave 11·7 c.c. nitrogen at 21° and 772 mm. N = 5·54.

$C_{14}H_{11}O_4N$ requires N = 5·45 per cent.

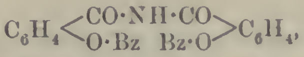
o-*Salicylsalicylamide* melts at 157°, but solidifies in the course of a few seconds owing to rearrangement to disalicylamide, which then melts at 200°. It is readily soluble in alcohol or hot benzene, moderately so in ether, sparingly so in light petroleum or cold benzene; it crystallises from benzene in colourless plates. Its alcoholic solution gives with aqueous ferric chloride an intense red colour, which changes to violet on diluting with water. *O*-Salicylsalicylamide is quantitatively rearranged to disalicylamide on boiling with water. It is readily soluble in pyridine, and the solution gradually acquires a yellow colour owing to the formation of disalicylamide, and the rearrangement is complete in six days. Aqueous alkalis dissolve it rapidly, yielding a yellow solution from which disalicylamide is precipitated on acidifying; in the case of sodium hydroxide, the sparingly soluble orange salt of disalicylamide is first formed and dissolves on dilution. *O*-Salicylsalicylamide is rapidly decomposed by cold, strong sulphuric acid into salicylamide and salicylic acid (compare behaviour of its isomeride with strong sulphuric acid). Its constitution follows from the close similarity between its properties and those of *o*-benzoylsalicylamide (*loc. cit.*).

Disalicylamide, 
$C_6H_4<\genfrac{}{}{0pt}{}{CO\cdot NH\cdot CO}{OH\qquad HO}>C_6H_4$.

Disalicylamide was prepared by boiling finely-powdered *O*-salicylsalicylamide with fifty times its weight of water for fifteen minutes, when it was obtained as a very bulky, white, fibrous mass melting at 200°; this crystallised from alcohol in yellow needles melting at 203°, the properties of which agree in all respects with those ascribed to disalicylamide by Schulerud and by G. Cohn (*loc. cit.*).

Disalicylamide is sparingly soluble in hot glacial acetic acid, but prolonged boiling converts it into the readily soluble *O*-salicylsalicylamide. One gram of disalicylamide was completely dissolved by 10 grams of acetic acid after thirty minutes' boiling; the mixture of the isomerides obtained by cooling and precipitating with water contained 66 per cent. of *O*-salicylsalicylamide.

Disalicylamide is dissolved without change by cold, strong, sulphuric acid; it is decomposed into salicylamide and salicylic acid by heating it with strong aqueous ammonia in a sealed tube at 115° for four hours.

Dibenzoyldisalicylamide, 
$C_6H_4<\genfrac{}{}{0pt}{}{CO\cdot NH\cdot CO}{O\cdot Bz\quad Bz\cdot O}>C_6H_4$, is obtained in 70 per cent. yield by pyridine benzoylation of disalicylamide at $-15°$.

0 2608 gave 7·0 c.c. nitrogen at 23° and 770 mm. N = 3·07.
0·3006 „ 8·0 „ „ 20° „ 771 mm. N = 3·09.
$C_{28}H_{19}O_6N$ requires N = 3·01 per cent.

The description of this compound already given (*loc. cit.*) must be amended in so far as it yields disalicylamide on decomposition by sulphuric acid or sodium hydroxide.

ORGANIC LABORATORY,
UNIVERSITY OF LIVERPOOL.

XXI.—*The Relation between Absorption Spectra and Optical Rotatory Power. Part I. The Effect of Unsaturation and Stereoisomerism.*

By ALFRED WALTER STEWART (Carnegie Research Fellow).

IN the course of some previous investigations, parts of which were carried out in conjunction with Mr. E. C. C. Baly, the author was able to show that a close relation exists between the absorption spectra and chemical reactivity of certain compounds. Up to the present time no attempt appears to have been made to correlate in a similar manner the absorption spectra of optically active substances with their rotatory powers ; and, as this research seemed likely to furnish results of some interest, the work was undertaken.

A change in the rotatory power of a compound may be brought about in many different ways, for example, by a change in temperature, by a change in the solvent in which the compound is dissolved when the observation is carried out, by the addition of certain inactive substances to the solution, &c. None of these examples, however, seemed to furnish a good test case ; and it was decided that in the first instance it would be best to compare the effects on the rotation and spectrum produced by a given series of changes in the constitution of certain substances. Now the simplest change in constitution which produces a well-marked effect on the chemical and physical properties of an organic substance is the change from the saturated to the unsaturated condition ; and since the question of stereoisomerism is closely allied to that of unsaturation, it was thought well to study these points together. The author has in preparation papers on the tartaric acids and similar isomerides ; and at a future date he hopes to study the question of the effect of solvents, mutarotation, and other branches of the subject.

It is well known that the degree of saturation of a carbon compound is closely connected with the rotatory power. Walden (*Zeit. physikal. Chem.*, 1896, **20**, 569) has made a detailed study of the point, and has shown that in general it may be said that a change from the saturated to the unsaturated condition in any compound produces a rise in rotatory power.* As the results obtained by Walden were sufficient for the purpose at present in view, it was only necessary to examine the absorption spectra of those compounds with which he had already dealt.

With regard to the relation between the absorption spectra of saturated and unsaturated compounds, reference may be made to papers by the following workers: Hartley and Huntingdon (*Phil. Trans.*, 1879, **170**, 257), Hartley (Trans., 1881, **39**, 153), Drossbach (*Ber.*, 1902, **35**, 1486), and Magini (*Nuovo Cim.*, 1903, [v], **6**, 343 ; *Phys. Zeit.*, 1904, **5**, 69).

The first question which presented itself was the effect of substituting a double or triple bond for a single linking. It is obvious that when two hydrogen atoms are removed from a compound, the molecule will undergo a profound change in constitution, and especially in those physical properties which are most intimately connected with the vibrations of the ether, such as the refractive index and the magnetic rotation. It has been shown by Walden that when a single bond is converted into a double one by the loss of two hydrogen atoms from the compound, the molecular rotatory power of the substance is increased. When the double bond is changed into a triple one by a further loss of two hydrogen atoms, the result was different; for, instead of rising again, the molecular rotatory power diminished, although it did not fall so low as that of the fully saturated compound. Walden's figures for the *l*-amyl esters of *β*-phenylpropionic, cinnamic, and phenylpropiolic acids are as follows:

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* He has since (*Zeit. physikal. Chem.*, 1906, **55**, 1) pointed out that the amyl alcohol used by him was not optically pure, but states that this in no way depreciates the value of his results for purposes of comparison with each other.

		$[M]^{20}_{D}$
β-Phenylpropionic ester	$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_5H_{11}$	+4·98
Cinnamic ester	$C_6H_5{\cdot}CH{:}CH{\cdot}CO_2{\cdot}C_5H_{11}$	16·36
Phenylpropiolic ester	$C_6H_5{\cdot}C{:}C{\cdot}CO_2{\cdot}C_5H_{11}$	12·05

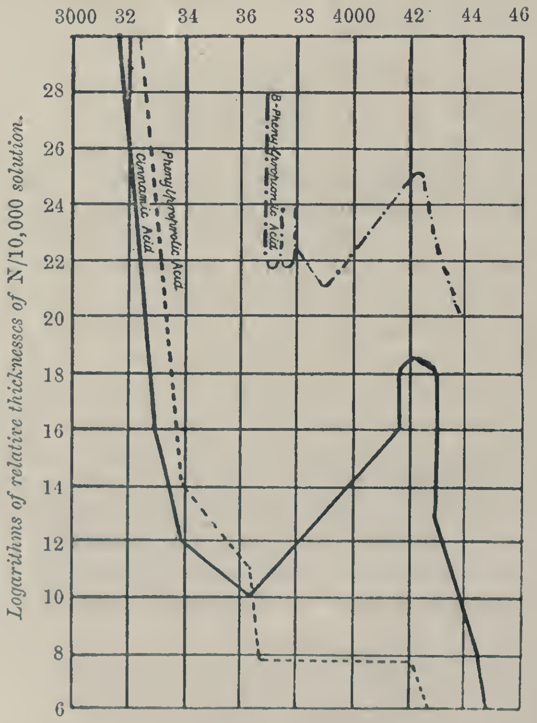
Now since the alcohol radicle is the same in each of these three substances, the change in rotation must be due to the change in the acidic part of the molecule. If further proof of this were necessary it is to be found in the work of Sir W. H. Perkin, who showed that the magnetic rotations of unsaturated acids were higher than those of the corresponding saturated substances. It is therefore clear that it is sufficient if we examine the spectra of the acids themselves; and it is not necessary to complicate their spectra with that of the amyl radicle.

The absorption curves of alcoholic solutions of *β*-phenylpropionic acid (see Baly and Collie, Trans., 1905, 87, 1344), cinnamic acid, and phenylpropiolic acid, plotted in the usual way, are shown in Fig. 1.

In his previous work, the author was concerned entirely with absorption bands in the spectra of substances; and, naturally, the first points which attracted attention in the spectra of the cinnamic series were the persistence and the position of the absorption bands which are shown in all three spectra. There seems, however, to be no connexion whatever between the bands and the optical rotatory powers of the three substances. If we consider the persistence of the absorption bands in the three cases we find that the cinnamic acid band has the greatest persistence; then come the bands in the *β*-phenylpropionic acid spectrum; and finally the phenylpropiolic acid band, which is so shallow that it appears as a mere extension of the spectrum at one dilution. This is not the order in which the rotations lie. Again, it might be supposed that the frequencies at which the heads of the bands are found might be in some way connected with the rotatory power. But this also is not the case; for the heads of the *β*-phenylpropionic acid bands lie, approximately, between 3700 and 3900, that of the cinnamic acid band at 3600, and that of phenylpropiolic acid is probably situated at a frequency of 3900.

It was evidently necessary to abandon the idea that the absorption bands were connected with the rotatory power, and to seek for other peculiarities in the spectra. Now if we leave absorption bands out of account, the only way in which substances can differ from one another in spectra is in their general absorptive power. We must therefore examine the three spectra with regard to the general absorption shown by each substance. Since Walden used the liquid esters without a solvent in his determination of the rotations, it will be well in the present case to examine the spectra of the three substances above the bands, since the effect of the solvent on the spectrum will probably be less marked in the more concentrated solutions.

Fig. 1.

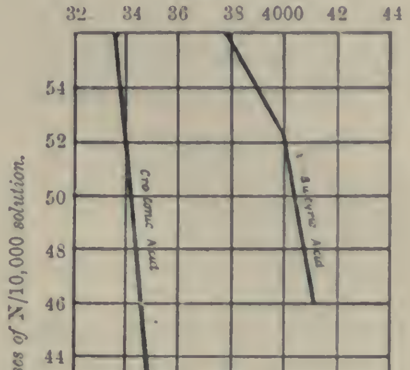


If we take the abscissa 26 as a convenient standard, we shall find that it is cut by the three curves in the following order: cinnamic acid, phenylpropiolic acid, and β-phenylpropionic acid. In other words, *the general absorptive powers of the three substances are related to* *one another in the same order as their molecular rotations.* The three curves cut the abscissa at the points shown below:

Cinnamic acid	3200
Phenylpropiolic acid	3300
β-Phenylpropionic acid.........	3700

There appears to be no close numerical relation between these numbers and the molecular rotations, but it should be borne in mind that such a numerical relation may exist at higher concentrations than are shown in the curves.

FIG. 2.



It seemed not improbable that the agreement in the foregoing case was merely an accidental one, and in order to see whether the rule was of more general application the spectra of several other acids were examined.

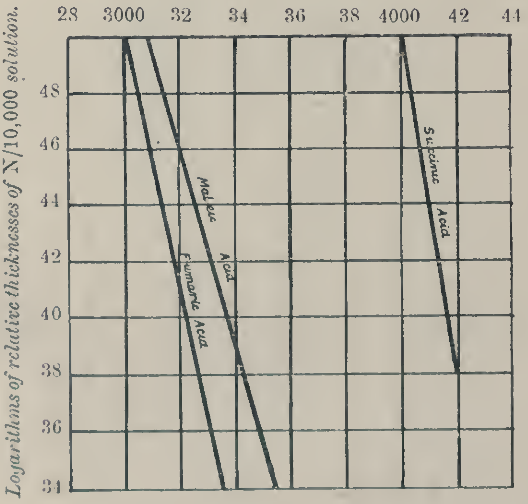
We have already dealt with a series of aromatic monobasic acids, so the next compounds which were examined were chosen from the aliphatic series. Walden, in the paper cited previously, gives the rotations of the *l*-amyl esters of *n*-butyric and crotonic acids as follows:

	$[M]^{20}_{D}$
Butyric acid, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot C_5H_{11}$	$+4 \cdot 43$
Crotonic acid, $CH_3 \cdot CH\colon CH \cdot CO_2 \cdot C_5H_{11}$	$6 \cdot 62$

The absorption curves of the two acids are shown in Figure 2. It is evident that here the same relation holds good as in the case of the other series; for crotonic acid, the ester of which has the greatest rotation, shows the greatest general absorption.

It must be pointed out that there is no relation between the two series, as series; for whilst amyl crotonate has a greater molecular rotation than amyl β-phenylpropionate, the absorptive power of crotonic acid is much less than that of β-phenylpropionic acid in solutions of equal concentration. The rule of "greater rotation, greater absorption," then, can be applied only in the case of compounds which contain chains of the same number of carbon atoms.

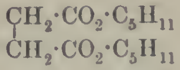
Fig. 3.



Having examined two series of monobasic acids, it seemed advisable to investigate the case of some dibasic ones. It will suffice for the present to give the results obtained with succinic and fumaric acids, the spectra of which are shown in Figure 3. Magini (*J. Chim. phys.*, 1904, 2, 410) has also examined the spectrum of maleic acid; his results are similar to those shown. The following figures are given by Walden:

$[M]_D$

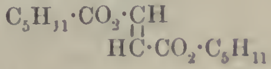
Succinic ester,



$$\begin{array}{l} CH_2\cdot CO_2\cdot C_5H_{11} \\ | \\ CH_2\cdot CO_2\cdot C_5H_{11} \end{array}$$

.. .. 9·71

Fumaric ester,



$$\begin{array}{l} C_5H_{11}\cdot CO_2\cdot CH \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad HC\cdot CO_2\cdot C_5H_{11} \end{array}$$

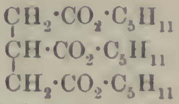
+15·17

Here, again, it is apparent that the same rule holds, for the absorptive power of the unsaturated acid is very much greater than that of the saturated acid.

It only remained to try two tribasic acids. The molecular rotations of the *l*-amyl esters of tricarballylic and aconitic acids have been determined by Walden:

$[M]_D^{20}$

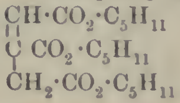
Tricarballylic ester,



$$\begin{array}{l} CH_2\cdot CO_2\cdot C_5H_{11} \\ | \\ CH\cdot CO_2\cdot C_5H_{11} \\ | \\ CH_2\cdot CO_2\cdot C_5H_{11} \end{array}$$

... +15·48

Aconitic ester,



$$\begin{array}{l} CH\cdot CO_2\cdot C_5H_{11} \\ \| \\ C\cdot CO_2\cdot C_5H_{11} \\ | \\ CH_2\cdot CO_2\cdot C_5H_{11} \end{array}$$

.... 23·66

and the curves of their absorption spectra are shown in Figure 4. In this case also the rule appears to hold.

If we turn to the case of series of homologous acids, the same rule which was applicable in other cases proves again true. When we examine the molecular rotatory powers of the amyl esters of homologous aliphatic acids, it is well known that a steady rise is shown as we go up the series; for example:

Amyl formate	+2·33
Amyl acetate	3·29
Amyl propionate	3·99
Amyl butyrate	4·25

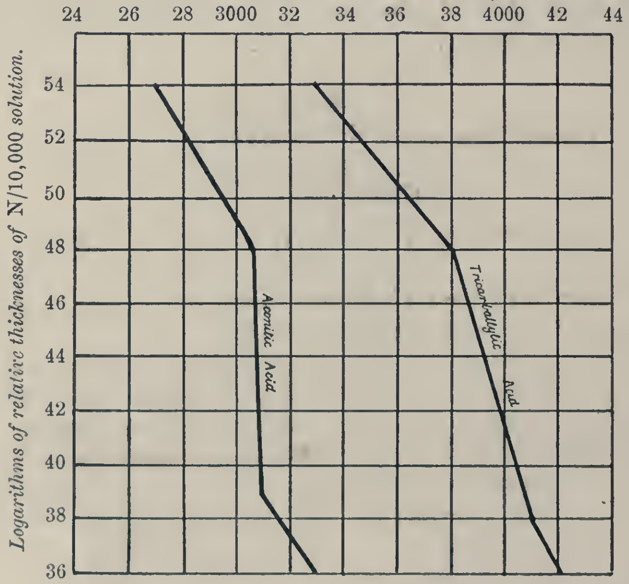
These figures were given by Guye and Chavanne (*Compt. rend.*, 1895, **120**, 452; *Bull. Soc. chim.*, 1896, [iii], **15**, 275). It is to be expected that, if the rule holds in this case, the acids corresponding to these esters will show a steady increase in general absorption; this has already been shown to be the case by Hartley and Huntington (*Phil. Trans.*, 1879, **170**, 257).

Since the rule holds good in the cases of all these various compounds, which differ to a very considerable extent in constitution, it seemed possible that it might be applicable in a slightly modified form to the case of stereoisomeric substances as well.

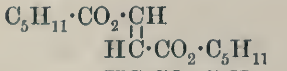
Walden (*Zeit. physikal. Chem.*, 1896, **20**, 377) has proved that the *l*-amyl esters of various stereoisomeric acids in the ethylene series have different specific rotations according as the maleinoid or fumaroid form of the acids is used. In general, there appears to be a difference of about four degrees between the molecular rotations of the two forms, the fumaroid form having the greater rotatory power. It appeared that, if this were the case, it should be possible to detect a difference in the spectra of the stereoisomeric acids, and several were therefore examined.

In the first place, we may consider the case of maleic and fumaric acids. The figures given by Walden for the rotations of *l*-amyl maleate and fumarate are as follows:

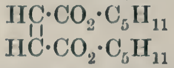
Fig. 4.



$[M]^{20}_{D}$



$$\begin{array}{l} C_5H_{11}\cdot CO_2\cdot CH \\ \quad\quad\quad\quad\quad\;\; \| \\ \quad\quad\quad\quad HC\cdot CO_2\cdot C_5H_{11} \end{array}$$ .... $+15\cdot17$

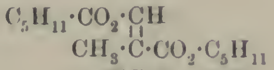


$$\begin{array}{l} HC\cdot CO_2\cdot C_5H_{11} \\ \;\; \| \\ HC\cdot CO_2\cdot C_5H_{11} \end{array}$$ .... $11\cdot82$

The absorption curves of these two acids are given in Figure 3, and an inspection of them will show that the rule "greater absorption, greater rotation" holds in this case also, for the curve of fumaric acid lies at a lower frequency than that of maleic acid.

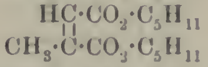
Figure 5 shows the absorption curves of mesaconic and citraconic acids. Since mesaconic acid shows the greater absorption, it is to be expected that its amyl ester will have a higher rotatory power than that of the citraconic ester. This is actually the case, as Walden's figures show:

$[M]_D^{20}$



$$\begin{array}{l} C_5H_{11}\cdot CO_2\cdot CH \\ \quad\quad\quad\quad\quad \| \\ \quad\quad CH_3\cdot C\cdot CO_2\cdot C_5H_{11} \end{array}$$

.... +16·01

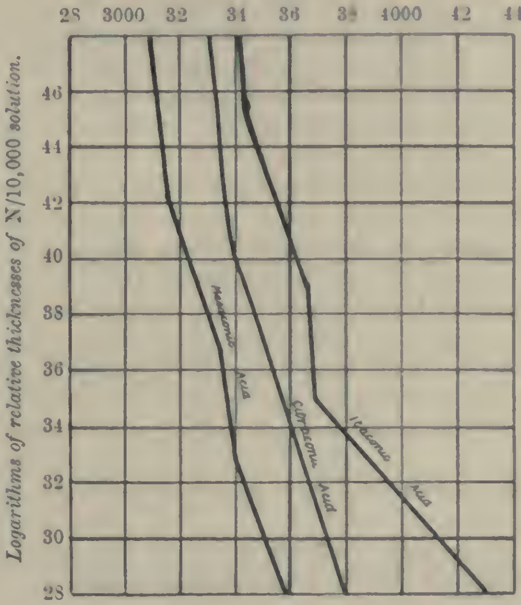


$$\begin{array}{l} HC\cdot CO_2\cdot C_5H_{11} \\ \quad \| \\ CH_3\cdot C\cdot CO_2\cdot C_5H_{11} \end{array}$$

.... 11·17

In the cases which have been described a comparison has been drawn between substances in which the atoms in the chain are linked together in the same manner in each isomeride; but at this point it may be well to indicate the results obtained when the unsaturation occurs at a different point in the chain. For this purpose it will be sufficient to quote the case of itaconic acid, which can be compared with the isomeric mesaconic and citraconic acids. The molecular rotation of itaconic diamyl ester has been found by Walden to be $[M]_D + 13{\cdot}42$. We might expect from this to find the absorptive power to lie between those of mesaconic and citraconic acids, but in point of fact it is less than either (Figure 5). We must therefore extend what has already been said with regard to unsaturation, and state the case in the following manner:

FIG. 5.



"If the spectra of a saturated and a corresponding unsaturated acid be compared, the acid corresponding to the amyl ester which has the greater molecular rotatory power will show the greater absorptive power; the same holds in the case of two stereoisomeric acids of the ethylene series; but it does not hold for structurally isomeric unsaturated substances."

Some of the results obtained in the course of this investigation are of interest from another point of view. It has already been proved by Magini (*J. Chim. Phys.*, 1904, 2, 410) that the spectrum of fumaric acid shows greater absorption than that of maleic acid; and in the present paper it is shown that a similar state of things is found in the case of the stereoisomeric, mesaconic, and citraconic acids. If this is a general rule, namely, if the more symmetrical molecule shows the greater absorptive power, one very interesting application of it may be indicated. In the case of certain stereoisomeric compounds, notably the hydrazones, no method of configuration determination has yet been devised; it seems probable that the absorption spectra of the two isomerides would show differences similar to those found in the case of the stereoisomeric acids, and a study of the absorption spectra of isomeric hydrazones might lead to some conclusions with regard to their configurations. In the case of certain stereoisomeric ethylene derivatives the configurations are still in doubt; for example, no real evidence has as yet been adduced in the cases of crotonic and *iso*crotonic acids, stilbene and *iso*stilbene, or the tolane dibromides. It is certain that some light might be thrown on the problem by an examination of their spectra. In the case of the various isomeric cinnamic acids the same method might yield results of some interest.

The following conclusions may be drawn from this part of the work:

I. Within certain well-defined limits, a close relation exists between the molecular rotatory powers of two substances and their absorption spectra.

II. The loss of two hydrogen atoms from a compound (by which a single bond is replaced by a double one) produces an increase in absorptive power as well as a rise in molecular rotatory power.

III. The loss of four hydrogen atoms (by which a single bond is changed to a triple one) also produces an increased absorption, though it has not such a great effect as the change from the single to the double bond. The same is true for the molecular rotation.

IV. In the case of stereoisomeric substances, the compound having the greater molecular rotation has also the greater absorption.

V. The same rule does not hold in the case of structure isomerides, at least in the unsaturated series.

VI. In homologous series, the compound having the greatest molecular rotation will have the greatest absorptive power.

In conclusion, the author wishes to express his thanks to Mr. Baly for his courtesy in lending his spectroscope, without which the work could not have been carried out.

The Spectroscopic Laboratory,
University College,
London.

XXII.—*Organic Derivatives of Silicon. Part II. The Synthesis of Benzylethylpropylsilicol, its Sulphonation, and the Resolution of the* dl-*Sulphonic Derivative into its Optically Active Components.*

By Frederic Stanley Kipping.

Some ten years ago, when carbon was the only element of which stable optically active derivatives had been isolated and examined, the author commenced an investigation of the organic derivatives of silicon, partly to extend our knowledge of the general behaviour and character of these compounds, but principally to obtain some of them in an optically active condition, that is to say, with the silicon atom at the centre of an asymmetric group.

At that time very little had been done with organic silicon compounds since the classical investigations of Friedel, Crafts, and Ladenburg, whose work, carried out no doubt under considerable difficulty, consisted principally in the study of some simple derivatives of silicon tetrachloride and of ethyl orthosilicate, which they prepared with the aid of sodium and zinc ethyl; later on, some of the corresponding propyl derivatives were obtained by Pape in a similar manner, and in the aromatic series Ladenburg had prepared phenylsilicon trichloride and other compounds closely related to it. Much more recently Polis (*Ber.*, 1885, **18**, 1542) had obtained tetraphenylsilicane* and a few similar compounds, and Reynolds had studied the action of silicon tetrachloride on some aromatic bases.

The choice of a suitable silicon compound, from which externally compensated derivatives might be obtained, being thus limited, the author's first experiments (Part I), which were carried out in conjunction with Lloyd (Trans., 1901, 79, 449), did not advance very far in the desired direction. Although a new way of preparing alkyl derivatives of silicon was found, and a number of new compounds—some of which were externally compensated—were obtained, the latter were found to be of little use for the principal object in view, owing to their instability.

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* This name is adopted here in preference to silicon tetraphenyl in order to show the analogy with the corresponding derivative of methane.

Other subjects for investigation having arisen, very little progress was made with silicon compounds until the autumn of 1903, when the author's discovery that silicon tetrachloride and magnesium alkyl and aryl halides would interact opened a new and wide field of research.* With the aid of these reagents, for which chemistry is so much indebted to Grignard, it seemed possible to prepare without very great difficulty a number of externally compensated silico-hydrocarbons and other compounds of a stable character, from which acid or basic derivatives could be obtained; the latter might then be resolved into their optically active components by the ordinary methods used in the case of carbon compounds.

The first task was to prepare a derivative of the type $SiR_1R_2R_3Cl$ by introducing successively three different hydrocarbon radicles in the place of three chlorine atoms of silicon tetrachloride; for this purpose it was important to choose carefully from among the various alkyl or aryl halides which might be employed because, as all the resulting compounds would certainly be liquids and could only be purified by fractional distillation, unless in every case the desired product differed sufficiently in boiling point from others which were formed in the reaction, its isolation would be impossible.

The preparation of methylethylsilicon dichloride, for example, would probably be a task of considerable difficulty; the product of the interaction of ethylsilicon trichloride and magnesium methyl bromide would doubtless be a mixture of the mono- and di-methyl compounds, and would contain also unchanged ethylsilicon trichloride; the isolation of the desired methylethyl derivative would consequently entail a long course of fractional distillation owing to the slight differences in the boiling points of the components of the mixture.

These considerations led to the investigation in the order given of the following series of reactions:

$SiCl_4 + MgEtBr = SiEtCl_3 + MgClBr$ (p. 214).

$SiEtCl_3 + MgPhBr = SiEtPhCl_2 + MgClBr$ (p. 215).

$SiEtPhCl_2 + MgPhBr = SiEtPhPrCl + MgClBr$ (p. 218).

and it was found that, although in every case by-products are formed in considerable quantities, the principal reaction proceeds as formulated above, and the desired product can be isolated without very much difficulty; the rigid exclusion of moisture during the whole series of operations is of course absolutely necessary.

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* Shortly after the publication of the author's preliminary note (*Proc.*, 1904, 20, 15), the preparation of some phenyl derivatives, by the interaction of silicon tetrachloride and magnesium phenyl bromide, was described by Dilthey (*Ber.*, 1904, 37, 1139; see also *Ber.*, 1905, 38, 4132).

The preparation of a suitable derivative of the externally compensated phenylethylpropylsilicyl chloride thus obtained seemed at first to offer no particular difficulty. The compound might react with the silver salt of an optically active acid, such as bromocamphorsulphonic acid, yielding a solid ester, which might possibly be resolved by fractional crystallisation; an experiment of this kind was tried, but the reaction seemed to proceed altogether abnormally (p. 220); at any rate, the initial product was either not the desired ester or else the ester was so unstable that it was useless for the purpose in view. Again, the interaction of the chloride and a primary or secondary base might yield a crystalline substance which, if sufficiently stable and if the base were optically active, might be resolved by fractional crystallisation. The few experiments which were made with *p*-toluidine seemed to show that a substituted amine of such a type, stable towards water, would not be obtained, a noteworthy fact considering the stability of the amines; this line was therefore abandoned.

These and other failures to obtain suitable derivatives from the chloride rendered it advisable to try and substitute another hydrocarbon radicle for the atom of chlorine. Judging from the behaviour of certain carbon compounds, such as triphenylmethyl chloride, which with zinc ethyl gives triphenylmethane and ethylene (E. and O. Fischer, *Annalen*, 1878, **194**, 259), it seemed probable that this reaction might not take the desired course. Contrary to expectation, however, phenylethylpropylsilicyl chloride was found to react with magnesium alkyl and aryl halides at moderate temperatures, giving a very fair yield of the tetra-substituted silicane, of which the two following representatives were prepared:

$$\mathrm{SiEtPhPrCl + MgMeI = SiEtPhPrMe + MgClI.}$$
$$\mathrm{SiEtPhPrCl + MgBzCl = SiEtPhPrBz + MgCl_2.}$$

Of these two silicohydrocarbons, only the latter so far has been studied, and the experiments have been almost exclusively directed towards its conversion into a sulphonic acid. It was thought that under suitable conditions this silicohydrocarbon might undergo sulphonation, either the phenyl or the benzyl radicle being attacked, in which case the sulphonic acid might then be combined with an optically active base, and the resulting salt resolved by fractional crystallisation.

An unforeseen and interesting result occurred on attempting to sulphonate with ordinary sulphuric acid, the phenylbenzylethylpropylsilicane being hydrolysed with separation of benzene and formation of *benzylethylpropylsilicol* or *benzylethylpropylsilicyl oxide*:

$$\mathrm{SiEtPhPrBz} + \mathrm{H_2O} = \mathrm{C_6H_6} + \mathrm{SiEtPrBz{\cdot}OH}.$$
$$2\mathrm{SiEtPrBz{\cdot}OH} = (\mathrm{SiEtPrBz})_2\mathrm{O} + \mathrm{H_2O}.$$

As far as could be ascertained, and the experiments seem to be conclusive, toluene is not produced under these conditions even in small quantities; the hydrocarbon which is obtained freezes readily, melts at about 4°, and has the properties of pure benzene (compare p. 223). Experiments with other compounds have also shown that there is a very great difference between the phenyl and benzyl radicles as regards their combination with silicon; the benzyl group, compared with the phenyl group, is held very firmly, and as far as the author's observations have gone it is not easily separated from the silicon atom by sulphuric acid even at moderately high temperatures, whereas the phenyl radicle is invariably displaced (compare also Part I, *loc. cit.*)

The silicol, which is probably the initial product of hydrolysis, or the oxide, which is formed from it in the manner just indicated, gradually undergoes sulphonation when, without first removing the benzene which has been formed, the heating with sulphuric acid at 100° is continued for some time; under these conditions there results a mixture of acids from which it was found to be very difficult to isolate a pure product, but ultimately a crystalline ammonium salt was obtained.

The mode of formation of this compound and the results of silicon determinations seemed to indicate that it was derived from an acid of the constitution $\mathrm{EtPrSi(OH){\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H}$, but the results of cryoscopic experiments in aqueous solution pointed to a molecular weight considerably higher than the calculated value. The *l*-menthylamine salt, prepared from the ammonium derivative, crystallised well; when examined by the ebullioscopic method in methyl-alcoholic solution it also gave values indicating a more complex molecular structure than that of a salt derived from an acid having the above constitution.

These results gave rise to some uncertainty as to the real nature of the parent sulphonic acid; on the one hand it seemed possible that the abnormal molecular weights might be ascribed to association conditioned by the hydroxyl- or sulpho-groups, especially as it had been found that simple silicones, such as benzylethylsilicone, EtBzSiO, are highly associated in solution; on the other hand, it seemed possible that the sulphonic acid might be derived from the oxide or ether of the molecular formula $\mathrm{BzEtPrSi{\cdot}O{\cdot}SiPrEtBz}$, as this compound might well be produced from the silicol previous to or during sulphonation, the oxide $Ph_3Si\cdot O\cdot SiPh_3$ being formed from triphenylsilicol even by the action of nitric acid (Kipping and Lloyd, *loc. cit.*).

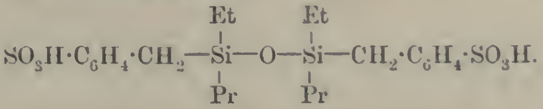
In the latter case, however, as the product would be a disulphonic acid, its salts, if highly dissociated in solution, would give molecular weight values but little higher than those calculated on a similar basis for the salts of the simple monosulphonic acid; the evidence obtained from the cryoscopic or ebulliscopic determinations therefore was inconclusive, although no doubt pointing to the more complex oxide formula rather than to that of the simple derivative of the silicol.

The results of analyses of the ammonium and of the *l*-menthylamine salts also indicated that the sulphonation product was a derivative of the oxide; although the percentage compositions calculated for the two possible formulæ differ but little (pp. 227, 229), and the presence of sulphur and nitrogen in the compounds renders the results rather less trustworthy than would otherwise be the case, the analytical data can hardly be reconciled with any other conclusion.

Other facts established during a series of experiments, which will form the subject of a later paper, may perhaps be mentioned here as having an important bearing on the constitution of this sulphonic acid. Firstly, when benzylethylpropylsilicyl chloride (Proc., 1905, 21, 65) is decomposed with water it gives a mixture of the silicol and the oxide, indicating that the former readily passes into the latter, even in presence of water.

Secondly, the sulphonation of the pure oxide with chlorosulphonic acid seems to give a mixture of acids similar to that obtained by the sulphonation of the silicol; at any rate, the products are in so far identical that they both contain the acid from which the crystalline ammonium- and *l*-menthylamine salts referred to above are derived.

It may be assumed, therefore, that the acid in question is a compound of the constitution



$$SO_3H\cdot C_6H_4\cdot CH_2-\overset{\text{Et}}{\underset{\text{Pr}}{Si}}-O-\overset{\text{Et}}{\underset{\text{Pr}}{Si}}-CH_2\cdot C_6H_4\cdot SO_3H.$$

This view necessitates the further assumption that the original sulphonation product is a mixture of two structurally identical but optically isomeric compounds, namely, the externally and the internally compensated acids; here again the experimental evidence, although not conclusive, is in conformity with this theoretical consequence, as the original sulphonation product is certainly a mixture. So far only the one acid has been isolated, but further experiments are in progress, and it is hoped that the other (or others) will be obtained ultimately in a condition of purity.

The acid which has been isolated, it may be stated at once, is an externally and not an internally compensated compound; although its *l*-menthylamine, *d*-bornylamine, and several other salts described in this paper seem to crystallise unchanged from various solvents under different conditions, the resolution of the acid is fairly easily accomplished with the aid of *d*-methylhydrindamine (Tattersall and Kipping Trans., 1903, **83**, 918).

The two substances obtained by fractionally crystallising the *d*-methylhydrindamine salt from aqueous methyl alcohol or from acetone differ widely in melting point and in outward properties, but have practically the same specific rotation in methyl-alcoholic solution; when separately decomposed with sodium carbonate and then converted into the *l*-menthylamine salts, they both yield compounds which, after recrystallisation, seem to have practically the same melting point and specific rotation as the *l*-menthylamine salt of the original *dl*-acid. In these circumstances, and especially as the specific rotations of the sodium salts of the optically active acids are very low, it was necessary to obtain confirmatory evidence that a resolution of the acid had in fact been accomplished; this evidence is given in detail in the experimental part (p. 236), and the enantiomorphous relationship of the resolution products is thereby conclusively established.

The present communication, however, is in some ways incomplete; for although the preparation of an optically active silicon derivative has been accomplished, the quantity of methylhydrindamine at disposal was so limited that the optically active compounds have so far only been prepared on a relatively small scale; their study will be continued, and the results will be published in the near future.

EXPERIMENTAL.

Preparation of Ethylsilicon Trichloride.

Silicon tetrachloride (50 grams), diluted with about three volumes of ether,* is placed in a large flask provided with a tap-funnel and a good stirrer, and after cooling in ice an ethereal solution of magnesium ethyl bromide ($1\frac{1}{6}$ mol.) is added slowly, the whole operation requiring about two hours. Even the first few drops of the ethereal solution produce a precipitate of magnesium chlorobromide with considerable development of heat, so that before the end of the experiment the contents of the flask consist of a thick, pasty mass which is difficult to stir; for this reason the solution of the magnesium compound should not be too concentrated.

After remaining for about twenty-four hours at the ordinary temperature, the ether is first distilled off and the flask is then slowly heated in an air- or oil-bath, the temperature of which is finally raised to about 200° and kept there until distillation ceases; towards the end of this operation an inflammable gas is evolved in considerable quantities.

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* Purified and dried with phosphoric oxide and with sodium.

The pale yellow, fuming distillate is then fractionated, as is also the mixture of ether, silicon tetrachloride, ethyl bromide, and ethylsilicon trichloride from the preliminary distillation; in these operations it is necessary to employ an efficient column,* otherwise the ether carries over a considerable quantity of ethylsilicon trichloride. The crude product is then again fractionated and the portion passing over between 97° and 103° collected separately; this fraction is pure enough for the preparation of other derivatives and usually weighs 30—35 grams; it is an almost colourless, fuming liquid having the properties described by Ladenburg.

The portions of the product collected above 103°, up to about 160°, doubtless consist of diethylsilicon dichloride, triethylsilicyl chloride, and possibly a little tetraethylsilicane; these are reserved for future investigation. The solid residue in the flask, after distilling off the crude product at 200°, is not pure magnesium salt, and when treated with water it yields a considerable quantity of a gelatinous substance, which glows when ignited.

In the first experiments on the preparation of ethylsilicon trichloride, with the aid of the Grignard reaction, magnesium ethyl iodide was used, but the yield of the desired product was very small, and on fractionally distilling, so much iodine was liberated that the side-tube of the flask sometimes became choked with crystals of the halogen.

Phenylethylsilicon dichloride, $EtPhSiCl_2$.

This compound is prepared by treating ethylsilicon trichloride in quantities of about 100 grams at a time with a slight excess ($1\frac{1}{10}$ mol.) of the theoretical quantity of magnesium phenyl bromide.

In order to avoid as far as possible the production of diphenyl during the interaction of the magnesium and phenyl bromide, the flask containing the magnesium and ether is provided with an efficient stirrer and cooled in ice as soon as the reaction has once started.

This solution is then added slowly, stirring vigorously, to the well-cooled ethylsilicon trichloride (b. p 97—103°); at first a slight turbidity is often produced, but otherwise no visible reaction occurs, and only a very small quantity of magnesium chlorobromide separates during the hour or two required for the addition of the ethereal solution. At the end of this time the liquid has the appearance of an emulsion, and, left at rest, it separates into two layers; the lower one then slowly deposits crystals and finally sets to a cake, when left at the ordinary temperature for about twelve hours. The precipitated magnesium salt is, however, rather gelatinous and difficult to separate by filtration, for which reason, and also to complete the reaction, the mixture is heated on a reflux condenser during a few hours, whereby the magnesium salt is rendered coarsely crystalline.

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* A 3—5 chamber column of the S. Young type.

The separation of the oily product from the magnesium salts in this and in many other preparations described later is accomplished in one of two ways: (1) The mixture is rapidly transferred to a large porcelain filter which is enclosed in an air-tight chamber formed from two desiccator covers placed mouth to mouth; the stem of the filter-funnel passes air-tight through the tubulure of the lower one into a filter-flask connected with an aspirator, so that dry air can be drawn into the chamber through a calcium chloride tube fitted in the tubulure of the upper cover and then through the filter. The liquid is thus separated by filtration, in absence of moisture, and the residual magnesium salt is repeatedly washed with the dry ether distilled from the oil. (2) The mixture is placed in an apparatus composed of two large bulbs connected together, on the principle of a fat-extractor, and so arranged that on heating the lower bulb the ether, which has filtered from the upper one, passes up the side tube to a condenser, and then flows back on to the pasty magnesium salt contained in the upper bulb, whence it passes through an asbestos filter into the lower one again; this form of apparatus is more suitable for working with large quantities.

The ethereal solution and washings having been combined, the ether is distilled, during which operation a further separation of magnesium salt sometimes occurs, even when the original mixture has been previously heated during some hours.

The yellow oily product is first submitted to a preliminary distillation from an ordinary flask; it begins to boil at about 40°, and the thermometer rises rapidly to about 200°; the principal portion passes over between this temperature and 240° and is collected separately. The pressure is then reduced to about 50 mm. and distillation continued as long as anything passes over, but even then there remains a considerable residue of a dark brown very viscid liquid, boiling above 300°, which has not been examined.

That portion of the distillate collected from 40° to 240° contains ether, ethylsilicon trichloride, bromobenzene, phenylethylsilicon dichloride, and diphenyl; it is repeatedly and systematically fractionated at the ordinary pressure in a flask provided with a neck 18—24 inches in length, in which is placed a Young's rod and disc column; corks and rubber are so rapidly attacked that an ordinary fractionating column fitted into a flask cannot very well be used.

The principal fractions of value finally collected from this portion of the distillate, starting from 100 grams of ethylsilicon trichloride, are: ethylsilicon trichloride, b. p. 97—103°, 5—10 grams and crude phenylethylsilicon dichloride, b. p. 228—232°, 40—50 grams.

The portions collected above 232° contain diphenyl in small quantities, this compound forming the main constituent of the fractions 255—265° which solidify on cooling. It is, in fact, the presence of diphenyl which necessitates so many distillations, and which renders it very difficult to prepare a pure specimen of phenylethylsilicon dichloride.

Many preparations of this compound have been examined; as the boiling point appeared to be 230—231° (760 mm. thread entirely in vapour), several specimens boiling at this temperature, at 227—228°, and at 229—230° have been collected and analysed, but were found to be impure, and to contain only about 30 per cent. of chlorine instead of the theoretical quantity, 34·5 per cent. That the impurity is diphenyl can be shown by submitting the samples to distillation in steam, when this hydrocarbon passes over, leaving *phenylethylsilicone.*

Pure phenylethylsilicon dichloride can only be obtained by repeatedly distilling the crude product (b. p. 228—232°) under different pressures and rejecting each time the very last portion of the distillate and any residue;* a sample thus obtained was analysed with the following result: †

Found Cl = 33·7. $C_8H_{10}Cl_2Si$ requires Cl = 34·5 per cent.

When freshly prepared it is a highly refractive, colourless liquid, but it turns pink, and frequently violet, after a very short time, these colours disappearing when the substance is heated. When kept for some weeks it generally becomes brownish-yellow, apparently owing to the liberation of traces of iodine; this is true of many of the di- and tri-substituted silicon tetrachlorides, but the state of combination of the iodine has not been ascertained. Phenylethylsilicon dichloride fumes strongly in moist air, and is at once decomposed by water, giving the corresponding silicone. It boils at 229—230° (760 mm.) and at 155—156° (100 mm.), thread entirely in vapour.

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* As an illustration of the difficulty of isolating the pure silicon compound, the following record may be given. A sample of the product (about 120 grams) boiling between 227° and 232° (760 mm.) was found to contain 30·4 per cent. of chlorine; it was distilled under atmospheric pressure three times, leaving about 5 grams of residue boiling above 230° after each operation; the percentage of chlorine rose from 30·4 to 31·8, 32·5, and 33·3 with each distillation. The sample was then distilled under a pressure of 100 mm., and the portion boiling at 155—156°, which formed more than 95 per cent. of the whole, collected; this gave 33·7 per cent. of chlorine, and on repeating the distillation under reduced pressure, leaving again about 5 per cent. as residue, this value underwent no appreciable change.

† In the analysis of this and of many similar compounds, the freshly distilled substance is dropped into a flask containing either water or a solution of silver nitrate and previously weighed, so that by re-weighing the amount of substance taken can be ascertained without giving any opportunity for absorption of atmospheric moisture; the halogen is then determined either volumetrically or gravimetrically.

That portion of the crude product boiling above 240° (atmospheric pressure) and collected by distilling under 50 mm. pressure contains diphenyl, *diphenylethylsilicyl chloride*, $SiEtPh_2Cl$, triphenylsilicyl chloride, $SiPh_3Cl$, and other compounds; the results of the investigation of these by-products will be published later.

Phenylethylsilicone, PhEtSiO.

This compound is obtained as a viscous, colourless oil when phenylethylsilicon dichloride is decomposed with water; a sample was extracted with ether, left for some time over sulphuric acid under reduced pressure, and then analysed with the following result:

0·1825 gave 0·0741 SiO_2; Si = 19·1.

$C_8H_{10}OSi$ requires Si = 18·9 per cent.

The compound is specifically heavier than water, in which it is practically insoluble; so far it has not been further examined.

Phenylethylpropylsilicyl Chloride, SiEtPrPhCl.

The gradual addition of an ethereal solution of magnesium propyl bromide to an equivalent quantity of phenylethylsilicon dichloride causes only a slight development of heat, so that cooling is, perhaps, unnecessary (as a rule ice was used), and the two liquids may be mixed fairly rapidly. The solution, when left overnight, deposits a considerable quantity of magnesium salt, but in order to ensure complete interaction, and to cause the gelatinous precipitate to become crystalline and granular, the mixture is first heated during some hours with reflux condenser, and then, after distilling off the ether, kept at 100° during three or four hours longer. The product is then separated from the magnesium salt with the aid of the distilled ether, in the apparatus already described, and the combined extract and washings are evaporated.

The remaining oil is first submitted to a preliminary distillation from an ordinary flask under reduced pressure (about 100 mm.) until the thermometer rises to about 210°, leaving in the flask a small quantity of an oil and a moderate quantity of magnesium salt, which separates during the process; the oily by-products of high boiling point are always formed in small quantities, and on distillation afford nothing of a definite character, the temperature rising slowly to about 350°. In this preliminary distillation almost the whole of the crude propyl derivative passes over between 175—190° (100 mm.), and this fraction, which is equal to about 90 per cent. of the phenylethylsilicon chloride employed, seems to be a fairly pure substance; when, however, it is submitted to systematic fractional distillation, using a long-necked flask fitted with a rod and disc column, it shows a wide range of boiling point. Under atmospheric pressure it begins to distil at about 240° and the temperature rises gradually up to about 265°, the greater part passing over between 250° and 260°; even after repeated operations the boiling point does not become very definite, and analyses of the product give unsatisfactory results. The first samples examined were collected between 250° and 260° and seemed to contain phenylethyldipropylsilicane, as they gave only 14—15 per cent. of chlorine instead of 16·6 per cent. which is required by theory.

When re-distilled under a pressure of 100 mm. with the same apparatus the product passes over from about 160° to 190°, but a very large proportion may be collected between 175° and 185°; systematic fractionation yields further quantities of substance boiling between the limits last mentioned, and when, finally, this liquid is again distilled two or three times, the main quantity passes over between 178° and 182°.

Chlorine determinations, made with samples thus collected, gave results agreeing with those required for the compound SiEtPrPhCl, namely 16·7 and 16·3 per cent., the calculated value being 16·6 per cent.

Phenylethylpropylsilicyl chloride is a colourless, refractive, mobile liquid, but it soon acquires a pink tinge, apparently owing to the liberation of traces of iodine. It fumes in the air and is readily decomposed by water, giving apparently a mixture of phenylethylpropylsilicol and the corresponding oxide, $(SiEtPrPh)_2O$.

Phenylethylpropylsilicol, SiEtPrPh·OH.

The product of the decomposition of phenylethylpropylsilicyl chloride with water has not yet been examined very carefully, but the corresponding silicol has been prepared by an indirect process.

In order to ascertain whether compounds of the type,

$$SiR_1R_2R_3\cdot NHR,$$

were or were not stable towards water (for if they were and could be obtained in crystals they might be employed for resolution experiments) the chloride mentioned above was treated with excess of *p*-toluidine in dry ethereal solution, and after filtering from the heavy precipitate of *p*-toluidine hydrochloride, the filtrate was washed with dilute acid, dried, and evaporated. The oil which remained was free from nitrogen and gave when warmed with sodium a vigorous effervescence; it was therefore distilled under atmospheric pressure, when it furnished a large fraction boiling from about 245° to 255°; above this temperature the thermometer rose very rapidly and the residue was not examined.

The fraction 245—255° was redistilled, the portion boiling at about 250° collected separately and analysed, with the following results:

0·1494 gave 0·3713 CO_2 and 0·1228 H_2O. $C = 67·8$; $H = 9·1$.
0·1512 ,, 0·3766 CO_2 ,, 0·1260 H_2O. $C = 67·9$; $H = 9·2$.
$C_{11}H_{18}OSi$ requires $C = 68·0$; $H = 9·3$ per cent.

Phenylethylpropylsilicol is a colourless, moderately mobile liquid practically insoluble in water; its further investigation has been deferred. The fact, established by this and by other experiments, that the union of nitrogen and silicon is dissolved in presence of water, renders such compounds unsuitable for the principal object of this investigation.

The Action of Phenylethylpropylsilicyl Chloride on the Silver Salt of Camphorsulphonic Acid.

Theoretically, the interaction of phenylethylpropylsilicyl chloride and silver *d*-camphorsulphonate (Reychler's acid) might be expected to give silver chloride and an ester,

$$SiEtPrPhCl + C_{10}H_{15}O{\cdot}SO_3Ag = AgCl + C_{10}H_{15}O{\cdot}SO_3{\cdot}SiEtPrPh.$$

Should this ester be crystalline, as seemed probable, it might be resolved by ordinary fractional crystallisation.

Experiments made on these lines seemed to show that the interaction proceeds abnormally. On adding the dry silver salt in slight excess to a solution of the chloride in dry light petroleum, an immediate separation of silver chloride occurs and, on shaking, the solution becomes clear; if then it is decanted and kept in a desiccator over sulphuric acid it very soon deposits crystals of *d*-camphorsulphonic acid, the quantity of this acid increasing on the addition of more dry light petroleum. The clear solution then contains an oil, which, however, is certainly not the expected ester, as it can be distilled in small quantities under atmospheric pressure without charring appreciably. This being the case, the petroleum solution was washed with water (which removed only a very small quantity of camphorsulphonic acid), dried, and evaporated. The residue consisted of a mobile oil and was distilled under reduced pressure (about 75 mm.); about half of it passed over from 175—185°, the thermometer then rose very rapidly to about 220° and the rest distilled from this temperature up to about 270°.

The principal fraction, after redistillation, was analysed:

0·1602 gave 0·3938 CO_2 and 0·1302 H_2O. C = 67·0; H = 9·0.
0·1476 „ 0·3684 CO_2 „ 0·1222 H_2O. C = 68·1; H = 9·2.

These results seem to show that this portion of the product consisted of phenylethylpropylsilicol; the other fractions were not examined, and a satisfactory explanation of the reaction cannot at present be given; it seems, however, from this, and from other experiments to be described in a later paper, that the ester is not produced, so that the further study of the reaction has been deferred.

Phenylmethylethylpropylsilicane, SiMeEtPrPh.

A small quantity of this silicohydrocarbon was prepared, principally in order to ascertain whether the displacement of the last atom of chlorine in the tetrachloride by an alkyl group offered any exceptional difficulties.

When phenylethylpropylsilicyl chloride is treated with an ethereal solution of excess of magnesium methyl iodide no appreciable reaction occurs, but on gradually heating in an oil-bath up to about 170°, allowing the ether to distil off, and then keeping at this temperature for about one and a half hours, a considerable separation of magnesium chloroiodide results. After cooling, adding water, and extracting with ether, the product is obtained as an almost colourless oil which distils almost entirely between 225° and 235° under atmospheric pressure.

Fractional distillation furnishes a liquid boiling constantly at 228—230° which forms about 70 per cent. of the crude product.

0·3830 gave 0·1190 SiO_2; Si = 14·6.

$C_{12}H_{20}Si$ requires Si = 14·8.

Phenylmethylethylpropylsilicane is a colourless, mobile liquid having a slight but pleasant aromatic odour; it is specifically lighter than water, in which, of course, it is practically insoluble.

Phenylbenzylethylpropylsilicane, SiEtPrPhBz.

This compound is formed by the interaction of phenylethylpropylsilicyl chloride and magnesium benzyl chloride, but its isolation is rather troublesome owing to the difficulty of separating it from the dibenzyl which is always produced in the preparation of magnesium benzyl chloride. This latter operation has been carried out under various conditions, but it seems impossible to prevent altogether the formation of the hydrocarbon; efficient cooling and stirring appear to be advisable. On adding phenylethylpropylsilicyl chloride to an ethereal solution of the magnesium compound no appreciable development of heat occurs and there is no separation of magnesium chloride; the ether is therefore distilled, and the residue gradually heated in an oil-bath to about 160°, at which temperature it is kept during about two hours.

The pasty product is then cooled, some ether added, and the solution filtered by the aid of the pump, the magnesium salt being subsequently well washed with ether; the combined filtrate and washings give on evaporation a yellow oil.

In the first preparations, this oil was submitted to distillation from an ordinary flask under atmospheric pressure, when, after many operations, it yielded a considerable quantity of a liquid boiling fairly definitely at about 325°, and some fractions of lower boiling point (which deposited crystals of dibenzyl) together with an oily residue. The substance boiling at 325° consisted of phenylbenzylethylpropylsilicane free from any appreciable quantity of impurity, as shown by the following analyses:

0·1386 gave 0·4093 CO_2 and 0·1102 H_2O. C = 80·5; H = 8·8.
0·1721 ,, 0·5102 CO_2 ,, 0·1369 H_2O. C = 80·8; H = 8·8.
0·1740 ,, 0·0380 SiO_2. Si = 10·3.
$C_{18}H_{24}Si$ requires C = 80·5; H = 8·9; Si = 10·6 per cent.

As the yield in the above case is small owing to the repeated distillations necessary to completely remove the dibenzyl, it is better to fractionate in the long-necked flasks provided with rod and disc columns (p. 216), which necessitates working under reduced pressure. At 100 mm., the dibenzyl passes over in the fractions collected from about 210 to 335°; these are cooled, the crystals of the hydrocarbon separated by filtration, and the liquid again fractionated as before. Repeating these operations several times, the phenylbenzylethylpropylsilicane is ultimately obtained boiling almost constantly at 249—251°, the yield being from 50—60 per cent. of the theoretical; in addition to dibenzyl, various by-products are obtained in the form of a yellow, fluorescent oil of very high and indefinite boiling point.

Analyses of the silicon preparations gave the following results:

0·1554 gave 0·4565 CO_2 and 0·1230 H_2O. C = 80·1; H = 8·8.
0·1704 ,, 0·5042 CO_2 ,, 0·1336 H_2O. C = 80·7; H = 8·7.
0·3830 ,, 0·0850 SiO_2. Si = 10·4.
0·2864 ,, 0·0649 SiO_2. Si = 10·6 per cent.

Phenylbenzylethylpropylsilicane is a colourless, highly refractive, rather viscous liquid, specifically lighter than water. The freshly distilled substance is quite clear, but when left in an open vessel it gradually becomes turbid, first at the surface and then downwards; this seems to be due to the condensation of moisture and is certainly not the result of the decomposition by moisture of some unchanged halogen derivative of silicon, as the product is free from halogen; when kept in a desiccator the silicohydrocarbon remains perfectly clear, It seems to be insoluble in ordinary concentrated nitric acid, but when left with it at the ordinary temperature the acid slowly becomes brown and the silicon compound changes into a tar, an odour of nitrobenzene being evolved; when added to a mixture of concentrated nitric and sulphuric acids the compound is violently attacked, a tarry product being formed. The behaviour of the substance towards these and other reagents is left for future investigation.

[*Decomposition of Phenylbenzylethylpropylsilicane with Sulphuric Acid.*

On adding the silicohydrocarbon just described to cold concentrated sulphuric acid ($1\frac{1}{2}$ vols.) and then shaking vigorously, a rise in temperature occurs and the acid becomes yellowish-brown, but after leaving the emulsion at rest for a few minutes an oil separates at the surface; this oil is insoluble in water and seems to be either unchanged phenylbenzylethylpropylsilicane, or a mixture of benzene, benzylethylpropylsilicol, and the ether or oxide of the latter, according to the exact conditions of the experiment.

The silicohydrocarbon is, in fact, first decomposed by sulphuric acid, probably according to the following equation,

$$\mathrm{SiEtPrPhBz} + \mathrm{H_2O} = \mathrm{SiEtPrBz{\cdot}OH} + \mathrm{C_6H_6},$$

and if the quantities used be large enough, and the shaking sufficiently vigorous, the spontaneous development of heat may ensure the decomposition of the whole of the silicohydrocarbon; if not, it is only necessary to heat the interacting substances at about 70° for a short time to complete the hydrolysis.

That benzene, and not its sulphonic acid, is thus produced is proved by the odour of the mixture, and also by the fact that on heating at 100° for some time a considerable loss in weight occurs, amounting to at least 20 per cent. of the silicohydrocarbon originally present; moreover, the benzene may be easily removed with a stream of dry air, collected in a well-cooled vessel, and identified by its melting and boiling points, or by converting it into *m*-dinitrobenzene, all of which methods were actually used; these experiments also showed that the benzene was free from toluene.

The whole or by far the greater part of the oil which remains floating on the sulphuric acid after the removal of the benzene is still insoluble in water; in one experiment a part of it was separated and analysed, with a result which indicated that it consisted principally of benzylethylpropylsilicyl oxide.

0·1645 gave 0·0510 SiO_2. Si = 14·6.

$C_{12}H_{20}OSi$ requires Si = 13·6

$C_{24}H_{38}OSi_2$,, Si = 14·2 per cent.

Further investigation is required to settle the nature of this product more exactly, but [it is obvious that the phenyl group has been removed from the silicohydrocarbon in the form of benzene.

Sulphonation of the Product with Sulphuric Acid.

From the statements just made it will be seen that the oxide, or mixture of alcohol and oxide, resulting from the above decomposition is not readily acted on by sulphuric acid at temperatures below about 70°; when, however, this product is heated with ordinary concentrated acid at 100°, shaking vigorously from time to time, it rapidly undergoes sulphonation.

The fact that the sulphonic acid is insoluble, or only sparingly soluble, in sulphuric acid and remains for the most part as an oil floating at the surface, is at first misleading, but on testing a portion of this oil after the heating has been continued for some time, it is found to be completely soluble in water and there is no separation of silica. The time required to complete the sulphonation seems to depend on whether or not the benzene (see above) is first removed; in any case, the presence of this hydrocarbon makes it appear that the reaction is incomplete (an oil separating on the addition of water), so that in the earlier experiments the heating with sulphuric acid was probably continued for a much longer period than was really necessary; judging from later experience, the character of the product was thereby materially changed.

The brief statements immediately following refer to experiments in which pure phenylbenzylethylpropylsilicane was heated with ordinary sulphuric acid ($1\frac{1}{2}$ vols.) at 100° during three to seven hours, and until a portion of the supernatant oil was soluble in water; in all cases a slight evolution of sulphur dioxide occurred towards the end of the process, and on diluting with water there resulted a pale yellow solution which showed a marked green fluorescence.

This solution was neutralised with ammonia, treated with excess of lead acetate and filtered from a heavy, sticky, flocculent precipitate consisting for the greater part of lead sulphate. Both the filtrate and the precipitate, when treated separately with hydrogen sulphide, gave solutions which yielded on evaporation a sulphonic acid of some silicon compound, but both these products were very viscous and gelatinous, could not be crystallised, and were of a dark brown colour owing to the presence of colloidal lead sulphide which it was found impossible to remove. They both gave with barium chloride sticky, flocculent precipitates which could not be purified, and with other metallic salts and with various organic bases they yielded either no precipitate or an oily product of an uninviting character.

The isolation of the sulphonic acid in the usual way, namely as lead or barium salt, being impracticable, the ammonium salt was utilised for this purpose.

The solution of the sulphonation product, after being neutralised with ammonia, is first evaporated on the water-bath as far as possible; alcohol is then added as long as a precipitate of ammonium sulphate is formed; the filtrate is again evaporated at 100° and treated with excess of methyl alcohol, to remove any ammonium sulphate which has escaped the first precipitation; after filtering again, the solution is practically free from sulphate, and the method here described has been found particularly useful in isolating several sulphonic acids, which give insoluble lead and barium salts, but the ammonium salts of which are soluble in alcohol.

The crude ammonium salt, obtained by evaporating the methyl-alcoholic solution, is a very viscid, pale yellow syrup, hygroscopic, and very readily soluble in water; with barium chloride it gives a flocculent, sticky precipitate which is practically insoluble in water and in strong alcohol, but which dissolves completely in warm aqueous alcohol. This precipitate is doubtless a mixture; when fractionally precipitated by adding water to its hot solution in aqueous alcohol, it yielded a colourless, granular barium salt, samples of which gave on ignition with sulphuric acid 47—50 per cent. of residue (barium sulphate and silica), the theoretical quantity required for the barium salt of an acid of the composition

$$\mathrm{SiEtPr(OH)\cdot CH_2\cdot C_6H_4\cdot SO_3H}$$

being 49·6 per cent.

A pure ammonium salt, however, can be isolated from the syrupy mixture as shown below.

Ammonium Sulphobenzylethylpropylsilicyl Oxide,
$\mathrm{(SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3\cdot NH_4)_2O}$.

The well-dried syrupy ammonium salt is dissolved in a little methyl alcohol, and ethyl acetate gradually added to the solution; this causes the separation of a yellow, buttery mass. The solution is decanted, the residue redissolved in a little methyl alcohol, and again precipitated with ethyl acetate; on repeating these operations the precipitate gradually becomes granular, and finally separates in lustrous crystals, but owing to the hygroscopic nature of the impurities first associated with it, anhydrous solvents must be used and access of moisture excluded as far as possible by crystallising over sulphuric acid; the mother liquors from these operations contain another ammonium salt which is referred to later (p. 228).

The pure ammonium salt obtained in this way is colourless, and to the unaided eye it appears well-crystallised,* but under the microscope it is seen to consist of thin, ill-defined plates. It is extremely soluble in water and alcohol, but practically insoluble in anhydrous acetone and ethyl acetate; when placed in cold water it first changes into a gelatinous mass, which dissolves only slowly, and the solution resembles soapy water in its great tendency to froth when shaken; with barium chloride the solution gives a crystalline precipitate readily and completely soluble in aqueous alcohol.

Silicon determinations were made with various samples, and the ammonia was estimated by distilling with caustic soda, the results agreeing fairly well with those required for the ammonium salt of a sulphonic acid of the composition $EtPrSi(OH)\cdot CH_2\cdot C_6H_4\cdot SO_3H$; that the sulphonic acid is really derived directly or indirectly from the alcohol $SiEtPrBz\cdot OH$, and not from the silicohydrocarbon,

SiEtPrPhBz,

is also clearly proved by the experiments already recorded (p. 223) as well as by those to be described later.

Molecular weight determinations were made by the cryoscopic method in aqueous solution, the following results being obtained:

Substance.	Solvent.	D.	M. W.
0·6514	20	0·130	476
0·6166	20	0·120	488
1·42	15·8	0·26	660

As the calculated molecular weight for a compound of the constitution $SiEtPr(OH)\cdot CH_2\cdot C_6H_4\cdot SO_3\cdot NH_4$ is 305, and as such a salt would probably be ionised to a considerable extent in aqueous solution, the experimental results were obviously not in harmony with those required for a substance of the above formula.

At first it seemed possible to attribute the abnormally high molecular weight to association, especially if the salt really contained a hydroxyl as well as a sulphonic group, but further investigations rendered this assumption improbable.

The fact that the mere decomposition of benzylethylpropylsilicyl chloride with water leads to the formation of a mixture of silicol and oxide, and that several other compounds of the type $SiR_3\cdot OH$ pass into the corresponding oxides, $(SiR_3)_2O$, very easily, pointed rather to the conclusion that the sulphonic acid in question was a derivative, not of the simple silicol, but of the corresponding oxide; the calculated molecular weight of the ammonium salt would then be 592. This supposition was also borne out by the following analyses of the ammonium salt itself, by analyses and molecular weight determinations of the menthylamine salt, and by other evidence which has been referred to in the introduction.

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* This was the first crystalline silicon compound obtained during at least six months' work, so the author has been careful not to overrate its beauty.

For the analyses the ammonium salt was dried at 100°; the samples may possibly have contained traces of ammonium sulphate, but were otherwise pure; this possible impurity could not be detected with the aid of barium chloride (see above). It is perhaps advisable to mention that a long layer of lead chromate and a long copper spiral were used in the combustions:

0·3107 gave 0·0623 SiO_2. Si = 9·5.
0·3630 ,, 0·0760 SiO_2. Si = 9·8.
0·5138 ,, 0·1025 SiO_2. Si = 9·3.
0·1934 ,, NH_3 = 5·7 (by distillation).
0·1864 ,, 0·3306 CO_2 and 0·1276 H_2O. C = 48·4; H = 7·6.
0·1552 ,, 0·2760 CO_2 ,, 0·1104 H_2O. C = 48·5; H = 7·9.
0·1760 ,, 0·3115 CO_2 ,, 0·1218 H_2O. C = 48·3; H = 7·7.
$C_{21}H_{44}O_7N_2S_2Si_2$ requires Si = 9·6; NH_3 = 5·7; C = 48·6; H = 7·4.
$C_{12}H_{23}O_4NSSi$ requires Si = 9·3; NH_3 = 5·5; C = 47·1; H = 7·5 per cent.

It will be seen from the calculated values that the salt derived from the oxide differs but little in percentage composition from that derived from the alcohol: all the analytical results, however, point in the same direction, namely, to the more complex formula. The determination of the silicon in the compound was accomplished by heating with concentrated sulphuric acid (Part I); when the salt is heated alone, even very slowly, as, for example, in carrying out the combustions, it yields a residue of silica of only about 3 per cent., a fact from which it might be inferred that unpolymerised silicon, or its oxide, is volatile at a red heat, or that some readily volatile silicon derivative is formed during the decomposition of the salt; a similar behaviour is exhibited by other silicon compounds of high molecular weight, as will be shown in a later communication.

It should perhaps be mentioned here that ammonium sulphobenzylethylpropylsilicyl oxide has been obtained by a method altogether different from that described above, and that some of the recorded analyses were made with samples of the salt prepared by this later method, the identity of the substances from the two sources having been fully established.

By-products formed during Sulphonation.

The crystalline ammonium salt described above is doubtless a pure substance; that is to say, it is free from the optically isomeric salt of the internally compensated acid, which theoretically should be formed by the sulphonation of the oxide.

When, however, the mother liquors from this crystalline product are evaporated over sulphuric acid, and again treated with anhydrous ethyl acetate, they give in the first place small quantities of the crystalline compound in an impure condition, and then deposits which, when dried, consist of a light colourless powder of microcrystalline structure; finally they yield a pale yellow gum which is readily soluble in ethyl acetate, but which is also an ammonium salt of a sulphonic derivative of silicon. The product of the sulphonation of phenylbenzylethylpropylsilicane with sulphuric acid under the conditions described above is, therefore, a mixture.

Apparently the proportion of the acid which furnishes the well-defined crystalline ammonium salt depends very greatly on the conditions of sulphonation, becoming smaller and smaller as the heating at 100° is continued, until at the end of about seven hours the powdery ammonium salt seems to be the principal, if not the only, solid product which can be isolated. As the latter seemed to be a mixture it was not analysed, but was converted into the *l*-menthylamine salt in the hope of obtaining a pure substance by fractional crystallisation; the menthylamine salt, however, proved on examination to be a compound of a very uninviting character, and a great deal of time was spent without any useful result; when fractionally precipitated from its solution in moist acetone or methyl alcohol by the addition of water, it gave colourless flocculent deposits of indefinite melting point. All these preparations lacked the characteristics of a pure compound, and their general behaviour indicated high molecular weight, that is to say, in comparison with the crystalline menthylamine salt described on page 229; having apparently no immediate bearing on the principal object of this investigation, they have been reserved for future examination.

Metallic Salts of Sulphobenzylethylpropylsilicyl Oxide

Hitherto the examination of the sulphonic acid has been entirely restricted to the question of its resolution, and very few derivatives of it have been prepared excepting salts of optically active bases; it has been incidentally observed that in addition to the ammonium salt the barium and sodium salts crystallise well, but these and other simple derivatives are reserved for future study. The barium salt, although practically insoluble in water and in alcohol, dissolves freely in aqueous alcohol, a remarkable property, which is also shown by barium salts of several other sulphonic derivatives of silicon.

l-Menthylamine Sulphobenzylethylpropylsilicyl Oxide,
$(SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N)_2O$.

The addition of an aqueous solution of *l*-menthylamine * hydrochloride to an aqueous solution of the crystalline ammonium salt (p. 225) produces at first an oily precipitate which dissolves on stirring, and when a certain proportion of the menthylamine salt has been added there results a viscid, translucent fluid very similar in appearance to raw white-of-egg; a further quantity of the hydrochloride then produces a crystalline precipitate, and finally the whole solution becomes a thick paste of crystals. The product is separated, washed, and recrystallised from aqueous methyl alcohol or from moist ethyl acetate.

It forms flat, lustrous plates or prisms, which when suddenly or very rapidly heated melt below 100° in their water of crystallisation; when slowly heated the melting point is about 230°, but as the salt decomposes a little at this temperature, the rate of heating probably influences the result to some extent. Although practically insoluble in water, it dissolves freely in the common alcohols, in aqueous acetone, and in moist ethyl acetate; in anhydrous acetone, ethyl acetate, and light petroleum it is practically insoluble.

Samples prepared by crystallising from aqueous methyl alcohol (I and II) and from moist ethyl acetate (III), and then dried in the air, contain four molecules of water of crystallisation, which is lost at 100°.

I. 1·0562 lost 0·0830 H_2O; $H_2O = 7·85$.
II. 0·6062 ,, 0·0464 H_2O; $H_2O = 7·65$.
III. 1·7577 ,, 0·1257 H_2O; $H_2O = 7·1$.
$C_{44}H_{80}O_7N_2S_2Si_2 + 4H_2O$ requires $H_2O = 7·5$ per cent.

Analyses of the anhydrous salt gave the following results:

0·4397 gave 0·0580 SiO_2. Si = 6·20.
0·3800 ,, 0·0525 SiO_2. Si = 6·51.
0·1655 ,, 0·3666 CO_2 and 0·1395 H_2O. C = 60·4; H = 9·4.
0·1591 ,, 0·3536 CO_2 ,, 0·1345 H_2O. C = 60·6; H = 9·4.
$C_{44}H_{80}O_7N_2S_2Si_2$ requires Si = 6·5; C = 60·8; H = 9·2.
$C_{22}H_{41}O_4NSSi$ requires Si = 6·4; C = 59·5; H = 9·2 per cent.

These results agree satisfactorily with those required for the menthylamine salt of a sulphonic acid derived from benzylethylpropylsilicyl oxide, and confirm the assumption that the acid is not benzylethylpropylsilicolsulphonic acid, the menthylamine salt of which would have the percentage composition shown above for the sake of comparison.

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* The optically pure *l*-base described by Tutin and Kipping (Trans., 1904, **85**, 65) was employed in all cases.

The equivalent of the salt was also determined by boiling a weighed quantity of the anhydrous substance with excess of *N*/50 sodium carbonate solution until all the menthylamine was expelled, and then titrating with *N*/50 acid, using litmus as indicator. The value obtained was 432·8, that calculated for the sulphonic derivative of the oxide being 434·4 against 443·4 for the simpler derivative of the alcohol. Control experiments made with pure menthylamine hydrochloride showed that this method of analysis admits of great accuracy, provided that the glass vessels used are carefully chosen.

The molecular weight of the *l*-menthylamine salt was determined in 99·6 per cent. methyl alcohol by Landsberger's modification of the ebullioscopic method, carefully dehydrated samples of the salt being employed; the following data were obtained:

Substance.	Volume of solution.	*E*.	M.W.
0·402	10 c.c.	0·08	578
0·61	5·5	0·245	520
1·15	8	0·4	413
1·01	15	0·155	500

Unfortunately the experimental error is very high owing to the exceptionally small value of the constant for methyl alcohol, and the results consequently are not by any means conclusive; taking the average value, which is about 503, and bearing in mind that the salt is probably ionised to a great extent, the result agrees fairly well with that which would be expected in the case of the menthylamine salt of the molecular formula $C_{44}H_{80}O_7N_2S_2Si_2$; the calculated molecular weight for this compound is 869, that of the salt derived from the silicol, 443.

The specific rotation of a sample of the menthylamine salt was determined in methyl-alcoholic solution: 0·402 gram of anhydrous salt; volume of solution, 25 c.c.; tube, 200 mm.; $\alpha - 0·5°$; $[\alpha]_D - 15·5°$.

Fractional Crystallisation of the l-*Menthylamine Salt.*

Assuming that the acid, from which the crystalline ammonium and *l*-menthylamine salts are derived, contains two asymmetric silicon groups, it might be either the internally or the externally compensated compound; in the latter case, the *l*-menthylamine and other salts of optically active bases might be resolved into their components by fractional crystallisation.

As regards the *l*-menthylamine salt, apparently, this possibility has not yet been realised.

The salt crystallises well from aqueous methyl alcohol in lustrous flat prisms; similarly from aqueous acetone; systematic fractional crystallisation from these solvents at the ordinary temperature left it unchanged in appearance and in melting point. Fractional crystallisation from anhydrous ethyl acetate, containing a trace of methyl alcohol, at temperatures near to the boiling point of the solvent, also yielded negative results, as did also the use of acetone in the place of ethyl acetate.

Fractional precipitation of the compound from a solution of the sodium salt of the acid was also tried, but the two fractions were identical in appearance and in melting point.

The *l*-menthylamine salt, in fact, is so constant in properties that in the later experiments on the resolution of the acid it has been used as the starting point, as the standard, and as the means of regaining the acid in a state of established purity from other compounds.

In the light of subsequent experience it seems not impossible that this salt may really have been resolved in some of the experiments mentioned above, but that the two components are so similar as to appear to be identical; in view of this possibility the salt will be again examined in the near future.

d-*Bornylamine Sulphobenzylethylpropylsilicyl Oxide*, $(SiEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{19}N)_2O$.

In preparing this compound by gradually adding a solution of *d*-bornylamine hydrochloride * to a solution of the ammonium salt, the same phenomenon is observed as in preparing the *l*-menthylamine salt; that is to say, the precipitate first produced is soluble in excess of the ammonium salt, and after the addition of a certain quantity of the bornylamine compound the product closely resembles raw white-of-egg; further quantities of the hydrochloride then cause the separation of an oil which slowly solidifies, and which can be obtained in a pure state, but not in very well-defined crystals, by allowing its solution in aqueous methyl alcohol to evaporate slowly.

This salt melts and decomposes a little at 208—210°; it dissolves freely in alcohol, ethyl acetate, or aqueous acetone, but is only sparingly soluble in anhydrous acetone and practically insoluble in water; it undergoes hydrolysis by water to some extent, bornylamine being evolved when its aqueous solution is boiled.

Attempts were made to resolve this compound by fractionally crystallising it from aqueous methyl alcohol, from aqueous acetone, and from a mixture of acetone and ethyl acetate at the ordinary temperature; also by fractionally extracting the anhydrous salt with hot dry acetone, from which it separates on cooling in opaque nodules; also by fractionally crystallising from a hot mixture of acetone and benzene. No change in melting point was observed, and extreme fractions, obtained by the use of hot acetone, when examined optically gave the following results in methyl-alcoholic solution:

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* The author is indebted to Dr. M. O. Forster, F.R.S., for a supply of this salt.

Fraction I. 0·3992 gram; volume of solution, 25 c.c.; 200 mm. tube; $\alpha + 0{\cdot}30°$; $[\alpha]_D + 9{\cdot}6°$.

Fraction IV. 0·5233 gram; other conditions as above; $\alpha + 0{\cdot}42°$; $[\alpha]_D + 10{\cdot}0°$.

Cinchonidine Sulphobenzylethylpropylsilicyl Oxide.

Owing to the difficulty of establishing the purity of the ammonium salt, the *l*-menthylamine derivative was used as the starting point in the preparation of this and of some other salts described below. The pure menthylamine compound is decomposed with a very slight excess of the theoretical quantity of sodium carbonate, the liberated base distilled in steam, and the residual solution rendered faintly acid with acetic acid; this solution is then concentrated and employed directly for preparing other compounds, which afterwards may be reconverted into the ammonium or sodium and then into the menthylamine salt.

The addition of a solution of cinchonidine hydrochloride to a solution of the sodium salt causes the precipitation of a very thick oil, which at first redissolves on stirring, but which is finally obtained as a viscous mass, practically insoluble in water.

This product was extracted fractionally with warm aqueous methyl alcohol and also with aqueous acetone, but in all cases the solutions gave oily or stringy silky deposits when cooled in ice. The salt was therefore dried, dissolved in hot ethyl acetate, the solution mixed with dry acetone, and evaporated over sulphuric acid; this treatment yielded a deposit of white translucent nodules, and by repeating these operations several times the compound was separated into three fractions, all of which, however, melted at 148—150°.

The salt being readily soluble in chloroform it was next precipitated fractionally from this solvent by adding dry acetone, and the deposits were then systematically extracted with hot acetone in presence of a little chloroform; finally there resulted four main fractions, the first and fourth of which were dried at 100° and examined polarimetrically in methyl-alcoholic solution, the volume of the latter being 25 c.c.:

Fraction I. 0·2852 gram; 200 mm. tube; $\alpha - 1{\cdot}67°$; $[\alpha]_D - 73{\cdot}2°$.
" IV. 0·2771 " " $\alpha - 1{\cdot}62°$; $[\alpha]_D - 73{\cdot}1°$.

These values, confirmed by melting-point observations, seem to show that the salt has undergone no change; and further experiments likewise gave negative results.

This salt, like several others which will be described later, is easily crystallised in absence of water, but is almost invariably deposited as an oil from wet solvents, such as aqueous methyl alcohol or aqueous acetone. It is only very sparingly soluble—possibly insoluble—in anhydrous acetone, but in presence of traces of water it dissolves moderately easily, separating again as a white powder on evaporating over sulphuric acid; if the solution and deposit are then exposed to the air, the powder first changes into masses of small needles and ultimately dissolves owing to absorption of moisture. Occasionally the salt may be obtained in long transparent prisms by crystallising from moist acetone containing the right proportion of water.

Cinchonidine Hydrogen Sulphobenzylethylpropylsilicyl Oxide.

The salt just described, and in fact many of the alkaloidal salts which have been prepared by precipitation, may be converted into an "acid" salt with the aid of hydrochloric acid.

The (normal) salt, melting at 148—150°, is dissolved in methyl alcohol, the solution treated with excess of concentrated hydrochloric acid, and the alcohol evaporated; the cinchonidine hydrogen salt is thus obtained as a very viscous silky mass and is washed with water, in which it is practicably insoluble. It dissolves freely in methyl alcohol and in aqueous acetone, but separates again as an oil on diluting with water, or when the solutions are kept in an ice-chest and allowed to evaporate spontaneously. When the salt is dried at 100° it is obtained as a glass-like mass which is practically insoluble in dry acetone and only very sparingly soluble in anhydrous ethyl acetate; from its solution in absolute methyl alcohol it is precipitated by acetone in the form of a granular powder, which deliquesces if exposed to moist air before it is free from acetone; using these solvents a small quantity of the salt was separated into four fractions of approximately equal weights, and the melting points of the first three were compared; they all behaved in the same way, darkening from about 215° and decomposing completely at about 220°, when heated rapidly.

The decomposing point of the salt being rather indefinite, the most sparingly soluble fraction was decomposed with ammonia, and the *l*-menthylamine salt obtained from it by precipitation; after recrystallisation from ethyl acetate this preparation had the melting point of the original *l*-menthylamine salt. As this cinchonidine hydrogen salt crystallised so badly and seemed to be unchanged it was not further examined; experiments with much larger quantities of material will be made in the near future.

Strychnine Salt.

The precipitate first produced by a solution of strychnine hydrochloride in a solution of the sodium salt is redissolved on stirring, giving a heavy, streaky, opalescent fluid, from which a very viscous oil separates on adding further quantities of the hydrochloride. This product was fractionally extracted with hot water, in which it was almost insoluble, but all the extracts deposited an oil which did not separate in crystals from aqueous alcohol or acetone. The salt was therefore dried at 100° and the resulting brittle solid dissolved in a mixture of anhydrous ethyl acetate and acetone; on evaporating over sulphuric acid, the solution deposited a fine white powder, which was separated into three main portions by systematically crystallising from the same anhydrous solvents at the ordinary temperature. These portions were then crystallised separately from warm acetone.

The several fractions thus obtained seemed to be identical in outward properties, and the first and second, when heated simultaneously, melted at 205—208°, turning slightly brown; the third or most soluble fraction had a rather lower melting point, and was decomposed with ammonia and converted into the *l*-menthylamine salt, which, after having been crystallised from aqueous alcohol, melted at 226—228°; as this salt was not quite pure and its melting point was only a little lower than that of the salt of the *dl*-acid, it was inferred that the acid had not been resolved.

This strychnine salt is very readily soluble in alcohol, aqueous acetone, and hot ethyl acetate, but only sparingly so in anhydrous acetone; it is easily obtained in a solid state from anhydrous solvents, but separates as an oil if water be present.

Resolution of dl-*Sulphobenzylethylpropylsilicyl oxide.*

When a solution of the sodium salt of the *dl*-sulphonic acid, prepared from the pure *l*-menthylamine salt, is treated with a solution of *d*-methylhydrindamine hydrochloride (Tattersall and Kipping, Trans., 1903, 83, 918), there results an oily precipitate, soluble at first in excess of the solution of the sodium salt, giving a very thick translucent fluid; the addition of methylhydrindamine hydrochloride in slight excess then causes the separation of a heavy oil, which may be washed by decantation. When this oil is dissolved in aqueous methyl alcohol and the solution left for a day or two, it slowly deposits a fine white powder and ultimately sets to a thick paste of minute crystals; when separated and dried, this salt melts at about 170°, but when recrystallised from aqueous methyl alcohol its melting point rises rapidly, and after three or four operations the most sparingly soluble portion melts at about 205°.

This compound, and further crystalline deposits of lower melting point, having been separated from the mother liquors, the latter finally deposit an oil which does not solidify when kept for some days at the ordinary temperature; when roughly dried, this oil dissolves in anhydrous acetone and the solution, if kept over sulphuric acid, deposits a gelatinous solid, which is now only sparingly soluble in anhydrous acetone (some water having been removed); from this solvent the salt is obtained as a very friable, somewhat resinous solid, which sinters at about 128°, melting completely at 132—135°.

The very great difference between these salts in outward properties pointed to the conclusion that the acid had been resolved; the two compounds were therefore dried at 100° and examined polarimetrically in methyl-alcoholic solution, with the following results:

Sparingly soluble salt: I. 0·4552 gram; volume of solution, 25 c.c.; 200 mm. tube; $\alpha + 0{\cdot}57°$; $[\alpha]_D + 15{\cdot}6°$.

II. 0·4624 gram under the same conditions; $\alpha + 0{\cdot}59°$; $[\alpha]_D + 16{\cdot}0°$.

These two samples were different preparations.

More readily soluble salt: 0·5224 under the same conditions; $\alpha + 0{\cdot}65°$; $[\alpha]_D + 15{\cdot}6°$.

These values being identical within the limits of experimental error, the two salts were separately decomposed with sodium carbonate, the *d*-methylhydrindamine expelled, and the solutions neutralised with acetic acid;* the *l*-methylamine salt was then prepared from each solution, recrystallised, and examined.

That from the sparingly soluble *d*-methylhydrindamine salt melted at about 228° and seemed to be identical with the corresponding salt of the *dl*-acid; its specific rotation was determined in methyl-alcoholic solution: 0·465 gram; volume of solution, 25 c.c.; 200 mm. tube; $\alpha - 0{\cdot}56°$; $[\alpha]_D - 15{\cdot}1°$. That from the more readily soluble *d*-methylhydrindamine salt melted at about 230°, and seemed to be identical with the corresponding salt of the *dl*-acid; its specific rotation was determined in methyl-alcoholic solution: 0·674 gram; volume of solution, 25 c.c.; 200 mm. tube; $\alpha - 0{\cdot}9°$; $[\alpha]_D - 15{\cdot}8°$.

A mixture of the two menthylamine salts from the two methylhydrindamine salts melted at about 228°.

These persistently similar results given by the two *d*-methylhydrindamine salts, although not incompatible with the view that the acid had been resolved, made it necessary to search carefully for any other possible explanation or source of error; the experiments were therefore repeated, starting from carefully purified *l*-menthylamine salt as the source of the acid, and using a sample of *d*-methylhydrindamine hydrochloride, which had been repeatedly crystallised and which showed a specific rotation of $[\alpha]_D + 32{\cdot}7°$ in aqueous solution, a value a trifle higher than those, $[\alpha]_D$ 30·3°, 30·7°, 31·2°, previously recorded (Tattersall and Kipping, *loc. cit.*). The same two salts as before were obtained when the *d*-methylhydrindamine compound was crystallised fractionally as already described.

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* Both the solutions were opalescent owing to some slight decomposition having occurred; for this reason, they could not be examined polarimetrically with accuracy, and a few readings which were taken indicated optical activity in both cases.

The two d-*methylhydrindamine salts contain enantiomorphously related acids.*

The proof that the *dl*-silicylsulphonic acid had in fact been resolved with the aid of its *d*-methylhydrindamine salt was afforded by examining the behaviour of the acids in the resolution products towards *l*-methylhydrindamine.

When the sparingly soluble *d*-methylhydrindamine salt is repeatedly evaporated with ammonia in a shallow basin, the organic base is entirely expelled and the ammonium salt of the acid remains as a gummy mass, readily soluble in cold water; this solution gives with *d*-methylhydrindamine hydrochloride an oily precipitate, which begins to crystallise almost immediately and which is identical with the original sparingly soluble salt of the *d*-base; with a solution of *l*-methylhydrindamine hydrochloride, the ammonium salt also gives an oily precipitate, which, however, does not crystallise even when rubbed with a crystal of the sparingly soluble salt, but which in the course of about twenty-four hours gradually changes to a rather gelatinous solid, which ultimately crystallises and then melts at about 145°.

As the acid in the ammonium salt thus behaves differently towards enantiomorphously related bases, it must itself be enantiomorphous.

The more readily soluble *d*-methylhydrindamine salt melting at about 135° (which must not be regarded as free from its optical isomeride) contains an acid enantiomorphously related to that of the more sparingly soluble salt melting at about 205°. When the former is decomposed with sodium carbonate, the organic base expelled, the solution neutralised with acetic acid and treated with *l*-methylhydrindamine hydrochloride, there results an oily precipitate which soon crystallises; fractional separation of this salt from aqueous methyl alcohol yields a considerable quantity of a sparingly soluble product melting at about 205° and indistinguishable from the *d*-methylhydrindamine compound of like melting point.

Now this salt, melting at about 205°, which is a derivative of *l*-methylhydrindamine, when repeatedly evaporated with ammonia in a shallow basin, gives an ammonium salt which shows the following behaviour: with a solution of *l*-methylhydrindamine hydrochloride there results a precipitate which crystallises immediately and which is identical with the original salt of the *l*-base; with a solution of *d*-methylhydrindamine hydrochloride, however, there results an oil which only solidifies after many hours, giving a somewhat gelatinous mass.

This salt of *d*-methylhydrindamine melts simultaneously with the similar gelatinous salt of *l*-methylhydrindamine mentioned above, namely, at about 145°; from these experiments it is concluded that the two compounds are enantiomorphously related.

dl-*Methylhydrindamine* dl-*Sulphobenzylethylpropylsilicyl Oxide.*

If the two salts melting at about 205° and obtained as described above, the one from the *d*-base, the other from the *l*-base, be mixed together, the product, after recrystallisation, should be identical with the salt prepared by the combination of *dl*-methylhydrindamine with the original or *dl*-acid.

The latter compound had been superficially examined some time before the acid had been resolved; it was obtained as an oil on adding a solution of *dl*-methylhydrindamine hydrochloride to a solution of the sodium salt of the *dl*-acid, and then as a fine white powder by the spontaneous evaporation of its solution in aqueous methyl alcohol or aqueous acetone; its melting point had been recorded as about 160°, and no abnormal behaviour had been noted in making the ordinary two or three melting-point determinations.

A mixture of samples of the two salts melting at about 205° was made by merely grinding them together in approximately equal quantities; this mixture had a very indefinite melting point, ranging from about 176° to 182°. Equal quantities of the two salts were therefore dissolved in aqueous methyl alcohol and the solution allowed to evaporate; it deposited a fine white powder which when dried had a most irregular melting point, readings such as 170°, 167°, 187° being obtained with one and the same sample, and in nearly all cases these figures were only approximations, as the melting ranged over several degrees.

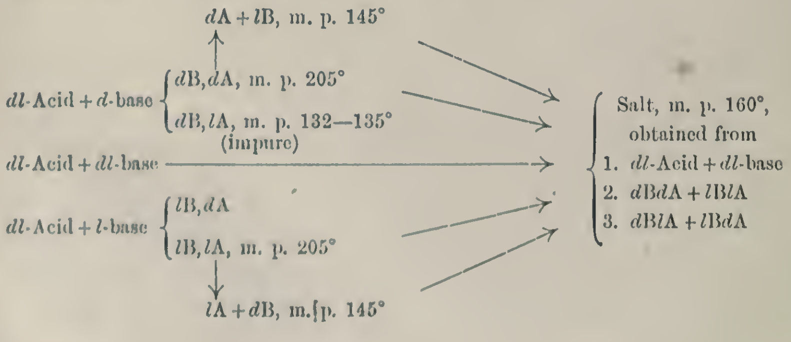
Now it is obvious that unless the mixture of the two salts melted at the same temperature (about 160°) as the salt of the *dl*-base, the two components of the mixture could not be enantiomorphously related, as supposed; the test was in fact a crucial one, and the observations were therefore continued. It was ultimately ascertained that the irregular behaviour of the mixture was caused by some change in crystalline form during the heating, for when the capillary tubes containing the mixture were plunged into the bath already heated at 160°, the substance melted immediately and completely (at least ten tubes tried); the two salts melting at about 205° did not show this behaviour when heated separately (at least ten tubes tried).

In examining the *dl*-methylhydrindamine salt of the *dl*-acid, prepared directly by precipitation, this particular behaviour had not been noticed, but clearly, if the above statements are true, this salt must behave exactly like the crystallised mixture of the two compounds melting at about 205°. A fresh sample of the salt was therefore prepared from the *dl*-base and the *dl*-acid and crystallised from aqueous methyl alcohol; when dried it sometimes melted at about 160°, but very often only sintered a little at this temperature and melted completely from 172° to 176°; when suddenly heated at 160°, however, it liquefied completely, just as did the artificially prepared salt of the *dl*-acid.

Assuming that the above experimental data are correct, and that the acid has really been resolved, the two salts melting at about 145° derived from the *d*- and *l*-bases if mixed together must also give a product identical with the *dl*-salt of the *dl*-acid; experiment confirmed this deduction.

Although the two compounds in question have so far been prepared on a test-tube scale only and very superficially examined, it was found that when they were ground together in approximately equal quantities they gave a powder which melted at about 167° when heated in the ordinary way, but at 160° when the tube was plunged into the bath at this temperature. The results of these experiments seem to prove conclusively that, in spite of the curious combination of indications to the contrary (p. 235), the *dl*-acid has been resolved into enantiomorphously related components; its resolution with the aid of *l*-methylhydrindamine, instead of the *d*-base, has been accomplished in a similar manner, but need not be described in detail.

The following summary of the more important experiments will perhaps afford the clearest view of the results:



The Resolution Products are Feebly Optically Active.

So many salts of the *dl*-sulphobenzylethylpropylsilicyl oxide and an even larger number of derivatives of benzylmethylethylpropylsilicanesulphonic acid * had been submitted to fractional crystallisation without obtaining the slightest indication of a resolution, that it was at first difficult to believe that the former acid had yielded finally when in combination with one of the active methylhydrindamines. This disbelief was certainly not lessened by the results of the preliminary study of the initial resolution products (*d*B*d*A, *dBlA*) or by optical examination of solutions of the small quantities of the active sodium salts which were first obtained, distinctly appreciable rotations being absent; it seemed advisable, therefore, to establish firmly the enantiomorphous relationship of the two acids in the manner described above, rather than to start the preparation of larger quantities of material for the exact determination of specific rotations.

For these reasons, but particularly because the available supplies of the active methylhydrindamines were very small, the optical constants of the acids have not yet been accurately ascertained; that the resolution products are indeed optically active is proved by the following experiments:

About 1·7 gram of the sparingly soluble *d*-methylhydrindamine salt melting at about 196° (and therefore not free from isomeride) was treated with excess of sodium carbonate and the organic base volatilised in a current of steam; when the escaping vapours ceased to show an alkaline reaction (the base is readily volatile) the solution was evaporated until it had a volume of about 15 c.c. This solution gave an average reading $\alpha + 0{\cdot}52°$, so that under these conditions, in presence of sodium carbonate, the sodium salt of the acid has a specific rotation of at least $[\alpha]_D\ + 3{\cdot}3°$.

About 1·7 gram of the *l*-methylhydrindamine salt melting at about 203° and practically free from isomeride was treated in a similar manner; the solution of the sodium salt showed a rotation of $\alpha - 0{\cdot}7°$, which corresponds with a specific rotation of about $[\alpha]_D\ - 4{\cdot}5°$.

It is perhaps scarcely necessary to add that the solutions were tested carefully to make sure that the activity was not due to the base. As, however, in the case of the above salts the activity is of the same sign as that of the base, one other experiment may be mentioned; a small quantity of the (impure) *d*-methylhydrindamine salt melting at about 135°, that is to say, the *d*B*l*A-salt was decomposed in a similar manner and the solution of the sodium salt examined; it showed a small but unmistakable rotation of about $\alpha - 0{\cdot}25°$.

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* These compounds will be described in a later paper.

The above value for the specific rotation of the *l*-acid is only given as an approximation, but it is probably not far from the true one; larger quantities of the *dl*-acid and of the two methylhydrindamines are being prepared, and it is hoped that a more complete description of the properties of the optically active acids and their derivatives may soon follow this communication.

In the earlier part of this work the author received help from Mr. A. E. Hunter, to whom he is indebted for the preparation of material.

The Committee of the Royal Society, having placed at the author's disposal several grants from the Government Fund, has thus rendered assistance for which the author desires to express his gratitude, and without which the present results could not have been obtained.

UNIVERSITY COLLEGE,
NOTTINGHAM.

XXIII.—*Derivatives of Multivalent Iodine. Part II. Action of Heat on* p-*Iodoacetophenone Dichloride,* p-*Iodoacetanilide Dichloride, and on the Dichlorides derived from* o-, m-, *and* p-*Iodotoluene.*

By WILLIAM CALDWELL and EMIL ALPHONSE WERNER.

IN a recent communication, one of us has shown (Werner, Trans., 1906, **89**, 1632) that when *p*-iodoacetophenone dichloride is gradually heated, a sudden decomposition takes place at about 94° accompanied by the evolution of much hydrogen chloride and a relatively small proportion of free chlorine; a similar phenomenon was also observed in the case of *p*-iodoacetanilide dichloride. New substituted derivatives were obtained, which, however, were only superficially examined; both decompositions have now been submitted to a detailed investigation, the results of which are recorded in the present paper.

The action of heat on iodochlorides has been hitherto generally considered to consist in the expulsion of the chlorine with regeneration of the original iodo-compound.

When *p*-iodoacetophenone dichloride is slowly heated in a current of air to a temperature not exceeding 130°, hydrogen chloride is abundantly evolved, whilst only 0·426 per cent. of chlorine is expelled in the free state; from the alcoholic solution of the residue, the new compound *ω-chloro-*p*-iodoacetophenone* is readily obtained in accordance with the equation:

$$CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2 = CH_2Cl{\cdot}CO{\cdot}C_6H_4I + HCl.$$

The constitution of this chloro-derivative is proved by the formation of *p*-iodobenzoic acid in almost theoretical amount when the compound is oxidised by chromic acid in glacial acetic acid solution.

When chlorine is passed into a chloroform solution of ω-chloro-*p*-iodoacetophenone, the *dichloride*, $CH_2Cl{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2$, is gradually formed, and when this compound is slowly heated, hydrogen chloride and much free chlorine are evolved, the latter amounting to 71·65 per cent. of the theoretical in accordance with the equation :

$$CH_2Cl{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2 = CH_2Cl{\cdot}CO{\cdot}C_6H_4I + Cl_2,$$

the remainder of the compound being decomposed with formation of the substitution derivative *ω-dichloro-*p*-iodoacetophenone*,

$$CHCl_2{\cdot}CO{\cdot}C_6H_4I.$$

This was isolated by fractional crystallisation of the residue first from alcohol, and subsequently from chloroform, in which it is much more soluble than the monochlorinated derivative.

On oxidation with chromic acid, it yields, like the parent substance, only *p*-iodobenzoic acid, proving that the hydrogen of the CH_2Cl group has been further replaced by chlorine.

When chlorine is passed into a chloroform solution of ω-dichloro-*p*-iodoacetophenone, the dichloride, $CHCl_2{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2$, quickly separates in pale yellow, glistening spangles ; this compound, when heated, evolves chlorine, and probably some hydrogen chloride, but it has not yet been obtained in sufficient quantity to examine its decomposition products in detail.

The preparation of *p*-iodoacetanilide dichloride has already been described (Werner, *loc. cit.*). When this compound is slowly heated in a current of air, it undergoes sudden decomposition at about 105° with abundant evolution of hydrogen chloride, whilst the amount of free chlorine evolved is only 1·11 per cent. The main result of the decomposition is the formation of *chloro-*p*-iodoacetanilide*,

$$(NHAc : I : Cl = 1 : 4 : 2 \text{ or } 3),$$

which is produced to the extent of 94—95 per cent. of the theoretical in accordance with the equation :

$$CH_3CO{\cdot}NH{\cdot}C_6H_4{\cdot}ICl_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_3ICl + HCl.$$

That the chlorine in this case has substituted hydrogen in the benzene nucleus only was proved by saponification of the anilide by heating with potassium hydroxide in methyl alcoholic solution to 130°, when it was quantitatively decomposed in accordance with the equation :

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_3ICl + KOH = CH_3{\cdot}CO_2K + C_6H_3ICl{\cdot}NH_2.$$

None of the chlorine was removed by the action of the alkali.

The chloroiodoaniline was precipitated as a white powder by pouring the product into water.

We have not yet ascertained the exact position of the chlorine in the chloroiodoaniline or its acetyl derivative; unless some change has taken place in the relative positions of the iodine and the acetylamino-group in the *p*-iodoacetanilide during the progress of the reactions, it is obvious that the chlorine must be limited to the position 2 or 3 in the benzene nucleus. We hope to investigate this point in the near future.

When chlorine is passed into a chloroform solution of chloro-*p*-iodoacetanilide, there is no separation of iodine, and the *dichloride*,

$$CH_3\cdot CO\cdot NH\cdot C_6H_3Cl\cdot ICl_2,$$

quickly separates in slender, bright yellow, glistening needles. This compound decomposes at 131°, evolving hydrogen chloride and free chlorine, the proportion of the latter amounting to 10·22 per cent.; this corresponds to a decomposition amounting to slightly over 50 per cent. of the theoretical, for the loss of two atoms of chlorine. The decomposition may be represented thus:

$$CH_3\cdot CO\cdot NH\cdot C_6H_3Cl\cdot ICl_2 \begin{array}{l} \nearrow CH_3\cdot CO\cdot NH\cdot C_6H_3ClI + Cl_2 \\ \qquad \text{Amounting to 52 per cent.} \\ \searrow C_8H_6ONCl_2 + HCl \\ \qquad \text{Substitution product amounting} \\ \qquad \text{to 48 per cent.} \end{array}$$

The composition of the substitution product formed has not yet been determined, want of material having prevented us from obtaining it so far in a state of purity, but a qualitative examination of a product melting at about 137°, and which contained some of the chloro-*p*-iodoacetanilide, gave evidence that the chlorine had in all probability effected a further substitution of hydrogen in the benzene nucleus.

The results obtained up to the present have revealed a very sharp difference in the decomposition of an aromatic iodochloride, according to the nature of the side chain present; thus when the group $CO\cdot CH_3$ is present the substitution of hydrogen by chlorine takes place in the methyl group of the chain only, whilst with the acetylamino-group, $NH\cdot CO\cdot CH_3$, present, the substitution takes place in the benzene nucleus. We hope to make further experiments in order to test how far this substitution may be carried by the aid of the iodochlorides.

In view of the results just recorded, we have been led to examine the action of heat on the dichlorides derived from the three isomeric iodotoluenes. These compounds have already been prepared by Willgerodt (*Ber.*, 1893, **26**, 358; Willgerodt and Umbach, *Annalen*, 1903, **327**, 269), but little attention has been paid to the action of heat on them, a mere record being given of the temperature at which the chlorides decompose, without any reference to the nature of the change. Thus *o*-tolyliodochloride is stated to decompose at about 91°, the *m*-tolyl compound at 104°, and the *p*-tolyl compound at about 85°, exploding at 100—118°.

We have made careful experiments on the action of heat on the three iodochlorides with the following results:

	First traces of Cl evolved.	Sudden decomposition (Cl + HCl evolved).	Percentage of free Cl evolved.	Percentage of theoretical for Cl_2.
o-$CH_3 \cdot C_6H_4 \cdot ICl_2$	66°	85—86°	4·07	16·5
m-$CH_3 \cdot C_6H_4 \cdot ICl_2$	70	88	1·75	7·11
p-$CH_3 \cdot C_6H_4 \cdot ICl_2$	92	110	3·21	13·03

It is readily seen from the numbers in the last column, which represent the percentage decomposition in accordance with the equation:

$$CH_3 \cdot C_6H_4 \cdot ICl_2 = CH_3 \cdot C_6H_4I + Cl_2,$$

that the main change in all three cases is that resulting in the formation of substitution products, in which we have recognised the presence of isomeric iodochlorides; the constitution of these is under investigation, and a full account of them is reserved for a separate communication.

So far, from *o*-tolyliodochloride we have obtained *o*-iodobenzyl chloride, the constitution of which was proved by oxidation to *o*-iodobenzoic acid by boiling with nitric acid, a small quantity of *o*-iodosobenzoic acid being produced at the same time. From *m*-tolyliodochloride, a chloroiodo-derivative has been prepared, which on oxidation with chromic acid in glacial acetic acid solution gives an acid melting at 210° and containing both chlorine and iodine. This is probably identical with the 2-chloro-3-iodobenzoic acid described by Smith and Knorr (*Amer. Chem. J.*, 1886, **8**, 95) melting at the same temperature.

From *p*-tolyliodochloride, *p*-iodobenzyl chloride has been obtained, the constitution being proved by the production of *p*-iodobenzoic acid on oxidation.

By the distillation of these products, we have separated at least one other substitution derivative in the case of the *o*- and *p*-compounds; the *m*-derivative appears to consist of only one compound.

Although the investigation of the three iodotoluene dichlorides is as yet far from complete, the results obtained up to this stage seem to show that in the case of *o*- and *p*-compounds the substitution of hydrogen by chlorine takes place chiefly in the side chain, whilst in the case of the *m*-compound the chlorine enters the benzene nucleus.

EXPERIMENTAL.

Action of Heat on p-*Iodoacetophenone Dichloride,* $CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2$.

The following method was generally adopted to determine the amount of free chlorine evolved. Two grams of the dichloride were slowly heated in a slow current of air, the evolved gases being drawn over water, and then through a wash bottle containing potassium iodide solution. This is necessary in order to prevent the hydrogen chloride from passing into the potassium iodide solution; otherwise too high a result is obtained. The free chlorine was estimated in each vessel.

Chlorine evolved = 0·00852 = 0·426 per cent.,

corresponding to only 1·9 per cent. of the theoretical decomposition for the loss of 2 atoms of chlorine; therefore 98 per cent. of the decomposition takes place with the formation of a substitution product.

Sixty grams were decomposed by heat, and the residue was purified by crystallisation from alcohol. Forty-two grams of the new compound were obtained in long, slender, almost colourless prisms melting at 126—127°.

0·2505 gave 0·3401 AgI + AgCl. Cl = 12·72; I = 45·55.

C_8H_6OClI requires Cl = 12·65; I = 45·27 per cent.

In order to prove the constitution of the compound, 7 grams were oxidised by boiling with the required amount of chromic acid in glacial acetic acid solution until carbon dioxide ceased to be evolved. On pouring the liquid into cold water 6·5 grams of a white, amorphous precipitate were obtained, which on crystallisation from alcohol yielded nacreous plates melting at 266°, the melting point of *p*-iodobenzoic acid.

0·2191 gave 0·2102 AgI. I = 51·82.

$C_7H_5O_2I$ requires I = 51·20 per cent.

When the original substance was heated with an alcoholic solution of sodium hydroxide, sodium chloride only was formed. The compound is therefore *ω-chloro-*p-*iodoacetophenone,* $CH_2Cl{\cdot}CO{\cdot}C_6H_4I$, formed in accordance with the equation:

$$CH_3{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2 = CH_2Cl{\cdot}CO{\cdot}C_6H_4I + HCl.$$

It is soluble in chloroform, benzene, or glacial acetic acid, but almost insoluble in water or dilute alkaline solutions.

*Action of Chlorine on ω-Chloro-*p-*iodoacetophenone,* $CH_2Cl{\cdot}CO{\cdot}C_6H_4I$.

Ten grams of ω-chloro-*p*-iodoacetophenone were dissolved in 150 cm. of chloroform; this gives a saturated solution at the ordinary temperature. When chlorine was passed into the solution no liberation of iodine took place, and after twenty minutes the *dichloride* separated in bright yellow, minute octahedra.

The product, amounting to 10·5 grams, was washed with chloroform and dried in the air.

0·5 gave with potassium iodide solution 0·1019 I. Cl = 20·38.

$C_8H_6OCl_3I$ requires Cl = 20·19 per cent.

Two grams of the dichloride were heated slowly, using the method and precautions already described. Evolution of chlorine commenced at 73°, and at 128—130° there was sudden decomposition with evolution of chlorine and hydrogen chloride.

Cl evolved, 0·2813 = 14·46 per cent., which corresponds to a decomposition amounting to 71·65 per cent. of the theoretical, in accordance with the equation: $CH_2Cl{\cdot}CO{\cdot}C_6H_4{\cdot}ICl_2 = CH_2Cl{\cdot}CO{\cdot}C_6H_4I + Cl_2$.

The decomposition is evidently accompanied by the formation of a substitution product. This was isolated in the following manner. The residue from the decomposition of 20 grams of the dichloride was dissolved in chloroform. The first crop of crystals which separated melted at 124—125°, and after recrystallisation proved to be the original ω-chloro-*p*-iodoacetophenone:

0·1848 gave 0·0923 AgCl. Cl = 12·35.

C_8H_6OClI requires Cl = 12·65 per cent.

The chloroform mother liquor was evaporated to dryness and the residue twice recrystallised from alcohol. Slender, satiny plates were obtained melting at 62—63°, and on analysis:

0·1671 gave 0·2737 AgCl + AgI, calculated for ratio 2AgCl + AgI. AgCl = 0·15045; Cl = 22·26; AgI = 0·12325; I = 39·85.

$C_8H_5OCl_2I$ requires Cl = 22·53; I = 40·31 per cent.

This compound is readily soluble in chloroform or benzene, from which it separates in thin plates. Five grams were oxidised by chromic acid mixture, the product poured into water, and the precipitate crystallised from alcohol, when nacreous plates of *p*-iodobenzoic acid separated. This was the only substance obtained, proving that the chlorine had again substituted hydrogen in the CH_2Cl group.

*ω-Dichloro-*p*-iodoacetophenone* also combines with chlorine, giving a dichloro-addition compound which separates from chloroform in pale yellow, glistening spangles. These decompose on heating, most of the chlorine being evolved in the free state.

0·17 gave, on trituration with potassium iodide, 0·03142 Cl. Cl = 18·48.

$C_8H_5OCl_4I$ requires Cl = 18·39 per cent.

This compound has not yet been produced in sufficient quantity to examine its decomposition products.

Action of Heat on p-*iodoacetanilide Dichloride*, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}ICl_2$.

Two grams of the dichloride were heated slowly in the manner already described:

Cl evolved = 0·022365 = 1·11 per cent.,

corresponding to only 5·2 per cent. of the theoretical; hence more than 94 per cent. of the decomposition is due to the formation of a substitution product. The residue from the action of heat on 20 grams of the dichloride was dissolved in hot alcohol, and on cooling slender, feathery needles separated, which were purified by further crystallisation. The compound separates from alcohol at first in needles, but after a few hours these change to small, hard, brilliant, four-sided prisms. The change is a physical one, inasmuch as both forms of crystals melt sharply at 144°.

0·6311 gave 26·8 c.c. nitrogen at 9° and 754·3 mm. N = 5·06.
0·2124 „ 0·272 AgI + AgCl. AgCl = 0·10309; Cl = 12·0; AgI = 0·16891; I = 42·96.

C_8H_7ONClI requires N = 4·73; Cl = 12·01; I = 42·97 per cent.

To determine the constitution of this substance 6 grams dissolved in methyl alcohol were heated in a sealed tube to 130° for two hours with 1·2 grams of potassium hydroxide dissolved in the minimum amount of water. The contents of the tube were poured into water, and the microcrystalline precipitate collected. The filtrate, which was neutral, contained potassium acetate, and was quite free from any halogen. The product of saponification, which was found to contain both chlorine and iodine, had all the properties of a base. It was obtained in crystals from alcoholic solution, and on analysis gave the following results:

0·2012 gave 0·2985 (AgCl + AgI). AgCl = 0·11315; Cl = 13·91; AgI = 0·1851; I = 49·77.

C_6H_5NClI requires Cl = 14·0; I = 50·09 per cent.

Chloro-p-*iodoaniline* crystallises from alcohol in clear, stout, strongly-refracting prisms melting at 73°. It readily forms a *picrate*, $C_6H_3ClI{\cdot}NH_2,C_6H_2(NO_2)_3{\cdot}OH$, which crystallises from aqueous solution in long, slender needles melting to a dark red liquid at 132°:

0·1974 gave 18·2 c.c. nitrogen at 10° and 758·5 mm. N = 11·1.

$C_{12}H_8O_7N_4ClI$ requires N = 11·398 per cent.

The *hydrochloride*, $C_6H_3ICl{\cdot}NH_2,HCl$, is precipitated on adding hydrochloric acid to an alcoholic solution of the base.

The *thiocarbamide*, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_3ClI$, is readily formed by warming the base with phenylthiocarbimide in alcoholic solution; it crystallises in slender, silky needles, which melt at 159°, and unlike most benzenoid thiocarbamides, it is only very slowly desulphurised on warming with an alkaline solution of lead.

Action of Chlorine on Chloro-p-*iodoacetanilide.*

On passing chlorine into a cold saturated chloroform solution of chloro-*p*-iodoacetanilide, there was no liberation of iodine, and the *dichloride* soon separated in slender, silky, bright yellow needles. These were washed with chloroform and dried in the air.

0·3014 gave, on trituration with solution of potassium iodide, 0·05822 Cl = 19·31.

$C_8H_7ONCl_3I$ requires Cl = 19·37 per cent.

The compound, when heated with the same precautions as adopted in previous experiments, decomposed at 131° with evolution of chlorine and hydrogen chloride:

1 gram gave 0·10224 Cl = 10·22 per cent.

This corresponds to a decomposition amounting to only 52·76 per cent. of the theoretical in accordance with the equation:

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_3Cl{\cdot}ICl_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_3ClI + Cl_2.$$

The remainder of the change is due to the production of a substitution derivative which, so far, has only been obtained in a partly pure state.

Action of Heat on the Chlorides of o-, m-, *and* p-*Iodotoluene.*

These compounds have been already prepared by Willgerodt (*loc. cit.*). In the case of *m*-iodotoluene, Willgerodt and Umbach prepared the dichloride in petroleum solution, no particular reason being given for the use of this solvent. They describe the compound as being slowly changed to a fuming liquid. We have experienced no difficulty in preparing it by passing chlorine through a solution of *m*-iodotoluene in chloroform, from which solvent the dichloride separated readily in a dense, crystalline form, hexagonal prisms predominating. The yield of the compound was very good when prepared in this way.

In the preparation of these iodochlorides generally we have found that a much more stable product is always obtained when a pure iodo-derivative is used. In some cases, when the iodo-compounds are not quite pure, a sudden, spontaneous decomposition of the dichloride may take place while suspended in the chloroform. This occurred in one or two instances. We have not known it to happen when the iodo-derivative used was quite free from impurity.

p-*Iodotoluene Dichloride*.—Two grams were heated in the manner already described. The first traces of chlorine were evolved at 92°.

At 110° there was sudden decomposition with the evolution of chlorine and hydrogen chloride.

Cl evolved = 0·064255 = 3·21 per cent.

This corresponds to only 13·07 per cent. of the theoretical decomposition for the loss of two atoms of chlorine; 87 per cent. therefore of the decomposition takes place in the formation of a substitution product.

p-Iodotoluene dichloride gradually decomposes on exposure to the air, and somewhat more rapidly when placed in a desiccator over sulphuric acid, hydrogen chloride only being evolved.

A sample which had been exposed to the air for four days gave Ci = 22·2.

$C_7H_7Cl_2I$ requires Cl = 24·56 per cent.

Some of the same sample after remaining four days over sulphuric acid gave Cl = 20·30.

One hundred and fifty grams of the dichloride were decomposed by heat. The resulting product, which was coloured by free iodine, was shaken with sulphurous acid solution and distilled in steam. A heavy, yellow liquid was obtained which was dried and analysed without any further purification:

0·2852 gave 0·4086 (AgCl + AgI). Cl = 13·43; I = 48·08.

C_7H_6ClI requires Cl = 14·06; I = 50·20 per cent.

In order to determine the constitution 10 grams were oxidised by chromic acid in acetic acid solution. The oxidation product was poured into water, and on crystallisation from aqueous alcohol, separated in nacreous plates melting at 264—265°. (*p*-Iodobenzoic acid melts at 266°.)

0·2172 gave 0·10668 I. I = 49·11.

$C_7H_5O_2I$ requires I = 51·2 per cent.

The presence of the chlorine in the side chain was confirmed by boiling the compound with sodium hydroxide in alcoholic solution. Chlorine only was removed by the alkali. The compound is therefore *p*-iodobenzyl chloride, $C_6H_4I{\cdot}CH_2Cl$.

This unites with chlorine in chloroform solution to form a *dichloride* which separates in slender pale-yellow needles.

0·5 gave 0·11395 Cl = 22·79.

$C_7H_6Cl_3I$ requires Cl = 21·94 per cent.

Two grams heated in the usual manner evolved chlorine at 50—53°. At 94—95° sudden decomposition took place accompanied with brisk effervescence, hydrogen chloride and free chlorine being evolved.

Cl evolved = 0·068 = 3·4 per cent.,

corresponding to 15·5 per cent. decomposition for the loss of 2 atoms of chlorine; hence 84·5 per cent. of the decomposition is accompanied by the formation of a substitution product.

o-*Iodotoluene Dichloride.*—Two grams of the compound were heated as already described. The evolution of the first trace of chlorine began at 66°. At 85—86° there was sudden decomposition with evolution of chlorine and hydrogen chloride.

Cl evolved = 0·814725 = 4·07 per cent.,

corresponding to only 16·5 per cent. of the decomposition for the loss of 2 atoms of chlorine; therefore 83·5 per cent. of the decomposition takes place with formation of a substitution product.

The product is a heavy oily liquid and contains both iodine and chlorine, but has not yet been quantitatively analysed. To determine the constitution, 5 grams of the oil were oxidised by boiling with nitric acid diluted with an equal volume of water. The product was purified by dissolving in boiling water and crystallising from aqueous alcohol, from which it separated in silky needles melting at 156° (*o*-iodobenzoic acid melts at 157°).

0·4355 gave 0·2015 AgI. I = 49·98.

$C_7H_5O_2I$ requires I = 51·2 per cent.

The mother liquor, which gave a yellow colour with sodium carbonate solution, contained a small quantity of a substance melting at 244° and having all the properties of *o*-iodosobenzoic acid.

The original liquid therefore consists chiefly of *o*-iodobenzyl chloride.

m-*Iodotoluene Dichloride.*—Two grams were heated as in the former cases. The first traces of chlorine were evolved at 70°, at 88° decomposition set in with brisk effervescence.

Cl evolved = 0·03493 = 1·746 per cent.,

corresponding to only 7·11 per cent. of the theoretical decomposition for the loss of two atoms of chlorine. Ninty-two per cent. of the decomposition, therefore, results in the formation of a substitution product. This was obtained as a heavy pale yellow liquid which after partial purification gave on analysis the following results:

0·475 gave 0·6658 AgCl + AgI. Cl = 13·2; I = 47·3.

C_7H_6ClI requires Cl = 14·06; I = 50·29 per cent.

This compound on oxidation yields an acid, melting at 210°, containing chlorine and iodine, and appears therefore to be 2-chloro-3-iodobenzoic acid.

University Chemical Laboratory,
Trinity College, Dublin.

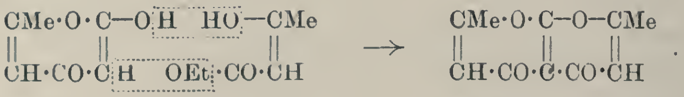
XXIV.—*The Condensation Products of Triacetic Lactone with Acetoacetic Ester and β-Aminocrotonic Ester.*

FREDERICK NOEL ASHCROFT FLEISCHMANN, M.A. Oxon.

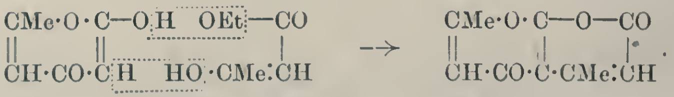
ALTHOUGH many members of the γ-pyrone series have long been known, no substance has hitherto been obtained containing two adjacent γ-pyrone rings. The possibility of such a substance being produced by the condensation of triacetic lactone with suitable reagents and the hope that its properties would throw some light on the constitution of the γ-pyrone nucleus led to this research.

With this object in view the reactions of triacetic lactone with ethyl acetoacetate and with β-aminocrotonic ester in presence of condensing agents were investigated.

The reaction between ethyl acetoacetate and triacetic lactone was examined first. Theoretically two different compounds might be formed by the complete condensation of the substances with the elimination of water and alcohol, (1) a γγ-dipyrone, (2) a γ-pyrone-lactone.

(1) 

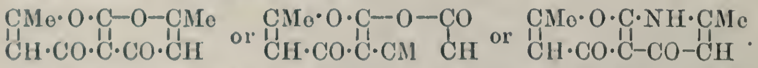
$$\begin{array}{l}\mathrm{CMe\cdot O\cdot C{-}O\,H\quad HO{-}CMe}\\ \|\qquad\quad\ \|\qquad\qquad\qquad\ \|\\ \mathrm{CH\cdot CO\cdot C\,H\quad OEt\cdot CO\cdot CH}\end{array}\longrightarrow\begin{array}{l}\mathrm{CMe\cdot O\cdot C{-}O{-}CMe}\\ \|\qquad\quad\ \|\qquad\ \ \|\\ \mathrm{CH\cdot CO\cdot C\cdot CO\cdot CH}\end{array}.$$

(2) 

$$\begin{array}{l}\mathrm{CMe\cdot O\cdot C{-}O\,H\quad OEt{-}CO}\\ \|\qquad\quad\ \|\qquad\qquad\qquad |\\ \mathrm{CH\cdot CO\cdot C\,H\quad HO\cdot CMe{:}CH}\end{array}\longrightarrow\begin{array}{l}\mathrm{CMe\cdot O\cdot C{-}O{-}CO}\\ \|\qquad\quad\ |\qquad\quad\ |\\ \mathrm{CH\cdot CO\cdot C\cdot CMe{:}CH}\end{array}.$$

One compound, however, only was formed which from the reactions of one of its derivatives was proved to be the pyrone lactone and not the dipyrone.

A completely analogous reaction takes place between triacetic lactone and ethyl β-aminocrotonate. In this case, if the condensation is complete, the production of a γγ-dipyrone or of a pyrone lactone with the elimination of ammonia and alcohol is possible, as is also the formation of a substance containing nitrogen in the second ring, with the elimination of water and alcohol.



$$\begin{array}{l}\mathrm{CMe\cdot O\cdot C{-}O{-}CMe}\\ \|\qquad\quad\ \|\qquad\ \ \|\\ \mathrm{CH\cdot CO\cdot C\cdot CO\cdot CH}\end{array}\text{ or }\begin{array}{l}\mathrm{CMe\cdot O\cdot C{-}O{-}CO}\\ \|\qquad\quad\ \|\qquad\quad\ |\\ \mathrm{CH\cdot CO\cdot C\cdot CM\quad CH}\end{array}\text{ or }\begin{array}{l}\mathrm{CMe\cdot O\cdot C\cdot NH\cdot CMe}\\ \|\qquad\quad\ \|\qquad\qquad \|\\ \mathrm{CH\cdot CO\cdot C{-}CO{-}CH}\end{array}.$$

On investigating the condensation, two substances were isolated, namely, the same substance as was formed when triacetic lactone and ethyl acetoacetate interact, and a substance containing nitrogen which, from its reactions, was shown to be a condensation product of two molecules of β-aminocrotonic ester with one of the lactone.

EXPERIMENTAL.

Condensation of Triacetic Lactone and Acetoacetic Ester.

The best condensing agent was found to be hydrogen chloride, the yield being nearly twice as much as when concentrated sulphuric acid was used, and several times greater than in the cases of acetic anhydride and piperidine.

Thirty grams of triacetic lactone and 60 grams of ethyl acetoacetate (theory 30·9) were dissolved in 300 c.c. of dry absolute alcohol, and the solution slowly saturated in the cold with dry hydrogen chloride. After standing for twenty-four hours the flask was filled with a fine mass of feathery crystals, which after being separated, washed with a little alcohol, and dried in a vacuum, weighed 10·6 grams. A further quantity was deposited by the filtrate on standing, the total yield after the solution had stood for fourteen days being 20·8 grams, or 44·3 per cent. of the theoretical quantity. The product was colourless and almost pure.

For analysis the substance was twice recrystallised from benzene; it then melted at 213—214° with decomposition.

0·1941 gave 0·4431 CO_2 and 0·0754 H_2O. C = 62·24; H = 4·31.
$C_{10}H_8O_4$ requires C = 62·50; H = 4·16 per cent.

The substance is readily soluble in chloroform or hot glacial acetic acid, moderately so in hot benzene or ethyl acetate, sparingly so in hot alcohol or ether, and insoluble in water or light petroleum.

Reactions of the Substance $C_{10}H_8O_4$.

The condensation product obtained in this way is extremely stable towards acids, with which, unlike dimethylpyrone, it forms no salts. It can be heated to a high temperature with strong sulphuric acid, forming a markedly blue fluorescent solution,* from which it can be recovered unchanged. In glacial phosphoric acid the fluorescence is but slight. The substance is not altered when boiled with a mixture of phosphorus tri- and penta-chlorides, and does not form an oxime or a hydrazone. On the other hand, it yields crystalline nitro- and monobromo-derivatives.

When heated with phosphorus and hydriodic acid in a sealed tube it

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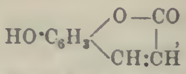
* This fluorescence is similar to that given by umbelliferone,  $HO\cdot C_6H_3\left\langle\begin{matrix}O-CO\\ CH{:}CH\end{matrix}\right|$, in strong sulphuric acid. The substance was subsequently proved to be of a similar type to that compound.

is entirely destroyed. With ferric chloride in alcoholic solution it gives a deep brown colour.

Reactions with Alkalis.—The behaviour of the substance towards alkalis is remarkable; definite salts, however, could not in all cases be prepared.

The substance dissolves in dilute sodium hydroxide forming a deep yellow solution; if the excess of alkali is considerable and the solution is boiled for a few minutes, it assumes a pale straw colour, and at the same time much decomposition takes place. Both solutions, however, yield the original substance on acidification.

With ammonia a deep yellow solution is likewise formed; if, however, the solution is evaporated on the water-bath the original substance begins to separate as soon as the excess of ammonia is removed.

An attempt to prepare a barium salt yielded rather better results, although owing to the instablity of the salt a pure substance was not obtained. About 5 grams of the substance were boiled with a large excess of barium hydroxide until the deep yellow solution first formed had assumed a pale straw colour. In the process a considerable quantity of carbonate was produced owing to decomposition. The excess of barium was removed by means of a stream of carbon dioxide and the solution filtered. The mother liquor was then evaporated to a syrup under reduced pressure and the syrup quickly filtered (to remove carbonate formed during the distillation) into a large volume of alcohol. An extremely hygroscopic white precipitate was obtained which was purified by solution in the smallest quantity of water possible and reprecipitation with alcohol. This was repeated several times, and the substance was finally dried in a vacuum.

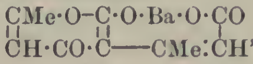
Found (mean of two analyses) Ba = 37·1.

$C_{10}H_8O_4Ba(OH)_2$ requires Ba = 37·7 per cent.

The *barium* salt decomposed on heating and on keeping. On acidification it yielded the original substance. A solution gave, on addition of a mercuric salt, an insoluble yellow *mercuric* salt; on addition of a mercurous salt the latter was educed. With silver nitrate a colourless insoluble salt was formed, which, however, was at once reduced on heating, giving a remarkably good silver mirror.

In these reactions it is clear that two types of salts are formed, namely, those giving the deep yellow solution and those produced from the latter by boiling. That neither of these two are normal salts of the free acid corresponding to the pyrone lactone (the original substance was subsequently proved to have that constitution) is shown in the first case by the yellow colour of their solutions and in the second from the analysis of the barium salt, for the normal salt would require only

24·8 per cent. of barium. Neither do they correspond to a type of salt represented by the constitution



$$\begin{array}{l}\mathrm{CMe{\cdot}O{-}C{\cdot}O{\cdot}Ba{\cdot}O{\cdot}CO} \\ \mathrm{CH{\cdot}CO{\cdot}C{-\!-}CMe{:}CH'}\end{array}$$

which requires 39·7 per cent. of barium and would be colourless.

Bromination of the Substance $C_{10}H_8O_4$.

Five grams of the substance were dissolved in hot glacial acetic acid, and to the solution 4·5 grams of bromine dissolved in glacial acetic acid were slowly added. The colour of the solution did not change on standing. On pouring into water, a white, voluminous precipitate was formed. This was crystallised from boiling alcohol and obtained in fine needles, which, on standing, changed completely to a mass of granular crystals. After drying in a vacuum, these melted at 191° with slight decomposition.

The yield was 5·2 grams, or 73·5 per cent. of the theoretical.

No dibromo-derivative was produced by using a larger quantity of bromine, but only a diminished yield of the monobromo-derivative was obtained.

For analysis the substance was recrystallised from benzene, from which it separated in brilliant needles containing benzene of crystallisation. This compound readily loses its benzene on heating or standing in the air.

1·4077 lost 0·1830. $C_6H_6 = 13·0$.

$(C_{10}H_7O_4Br)_2,C_6H_6$ requires $C_6H_6 = 12·6$ per cent.

The residue melted at 191°, and on analysis:

0·2056 gave 0·3317 CO_2 and 0·0489 H_2O. $C = 44·40$; $H = 2·63$.

0·2308 ,, 0·3714 CO_2 ,, 0·0573 H_2O. $C = 43·89$; $H = 2·75$.

0·2233 ,, 0·1565 AgBr. $Br = 29·76$.

$C_{10}H_7O_4Br$ requires $C = 44·28$; $H = 2·58$; $Br = 29·52$ per cent.

The substance, besides being readily soluble in hot benzene, is very soluble in chloroform or hot glacial acetic acid, moderately so in hot acetone, ethyl acetate, or alcohol, slightly so in light petroleum, and insoluble in water.

From glacial acetic acid, acetone, or alcohol, the fine needles first formed on crystallisation change to the granular condition on standing. The substance is also readily soluble in hot toluene, giving a compound similar to that obtained with benzene; on analysis:

1·5188 lost 0·2158. $C_7H_8 = 14·2$.

$(C_{10}H_7O_4Br)_2,C_7H_8$ requires $C_7H_8 = 14·5$ per cent.

When the bromo-derivative is boiled with zinc dust and acetic acid, it is converted into the substance $C_{10}H_8O_4$ (m. p. 213—214°) from which it was produced.

Nitration of the Substance $C_{10}H_8O_4$.

Three grams of the substance $C_{10}H_8O_4$ were dissolved in 10 c.c. of strong sulphuric acid and the solution cooled to 0°. To this solution a cold mixture of 2 c.c. of nitric acid, sp. gr. 1·2 (the theoretical amount for a dinitro-derivative), and 8 c.c. of strong sulphuric acid were slowly added. The temperature during the process was not allowed to rise above 4°. The mixture, which had become deep yellow and began to evolve gases, was then poured into 100 grams of a mixture of ice and water.

A slightly coloured precipitate was obtained which after filtration was crystallised from glacial acetic acid, when it separated in shining, yellow needles. The yield was 2 grams, corresponding to 55·7 per cent. of the theoretical.

The yield was not improved by using either more or less nitric acid. In an experiment in which the theoretical quantity was used the reaction was incomplete, whilst when a greater excess was employed or the temperature allowed to rise, decomposition ensued accompanied with a copious evolution of gases and a much diminished yield.

For analysis, the substance was recrystallised from ethyl acetate, from which it separated in pale yellow needles which began to darken at about 180° and melted with violent decomposition at about 200°.

0·3127 gave 16·7 c.c. moist nitrogen at 16° and 759·5 mm. N = 6·2.

$C_{10}H_7O_6N$ requires N = 5·9 per cent.

The substance is readily soluble in cold acetone, hot glacial acetic acid, ethyl acetate, benzene, or chloroform, slightly so in hot alcohol, and almost insoluble in ether, light petroleum, or water. With ferric chloride in alcoholic solution, a deep yellow colour is produced. With alkalis, it forms deep yellow to red solutions, and in the case of ammonia a further reaction takes place.

It is not attacked by hydrogen sulphide in boiling alcoholic solution, but is reduced, with elimination of the nitro-group, to the original substance, $C_{10}H_8O_4$, when boiled with zinc dust and acetic acid.

Reaction between Ammonia and the Substance $C_{10}H_7O_4{\cdot}NO_2$.—The nitro-derivative dissolves slowly in cold concentrated aqueous ammonia, giving a deep red solution which at once begins to deposit a colourless solid, the solution at the same time becoming pale yellow.

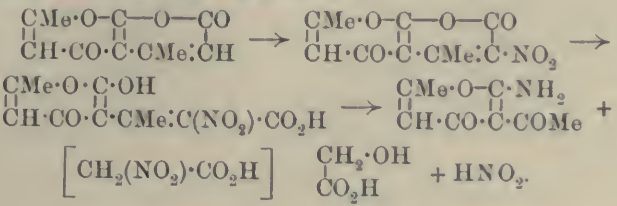
Five grams of the nitro-derivative were continuously shaken with 30 c.c. of aqueous ammonia (sp. gr. 0·88) until the original solid was entirely dissolved and the colour of the solution had changed to pale yellow. The colourless precipitate which had subsequently formed was filtered, washed with a little water, and dried in a vacuum: yield 2·5 grams.

The substance dissolved readily in hot water and the solution, when cooled slowly, set to a jelly, which on standing furnished a mass of fine crystals. For analysis, it was recrystallised from hot water and dried in a vacuum:

0·1947 gave 14·7 c.c. moist nitrogen at 18·5° and 755 mm. N = 8·65.
0·1977 ,, 14·8 c.c. ,, ,, ,, 18° ,, 757 mm. N = 8·62.
$C_8H_9O_3N$ requires N = 8·38 per cent.

An examination of the properties of this substance and a comparison with those of aminodehydracetic acid prepared by the action of strong aqueous ammonia on dehydracetic acid (Oppenheim and Precht, *Ber.*, 1876, **9**, 1100; Collie and Myers, Trans., 1893, **63**, 128) proved the identity of the two substances. The substance here described melted at 208° (uncorr.) whilst aminodehydracetic acid melts at 208·5° (corr.) (O. and P.).

The mother liquor from the preparation of this substance gave on acidification the reaction for nitrous acid with potassium iodide and starch. This reaction therefore affords a proof of the constitution of the series of substances in question, and fixes the position of the nitro-group in the nitro-derivatives, for, of the two possible types of condensation products, that containing the lactone ring is the only one which could yield aminodehydracetic acid:



$$\begin{array}{l}\text{CMe}\cdot\text{O}-\text{C}-\text{O}-\text{CO} \\ \text{CH}\cdot\text{CO}\cdot\text{C}\cdot\text{CMe}{:}\text{CH}\end{array} \longrightarrow \begin{array}{l}\text{CMe}\cdot\text{O}-\text{C}-\text{O}-\text{CO} \\ \text{CH}\cdot\text{CO}\cdot\text{C}\cdot\text{CMe}{:}\text{C}\cdot\text{NO}_2\end{array} \longrightarrow$$

$$\begin{array}{l}\text{CMe}\cdot\text{O}\cdot\text{C}\cdot\text{OH} \\ \text{CH}\cdot\text{CO}\cdot\text{C}\cdot\text{CMe}{:}\text{C(NO}_2)\cdot\text{CO}_2\text{H}\end{array} \longrightarrow \begin{array}{l}\text{CMe}\cdot\text{O}-\text{C}\cdot\text{NH}_2 \\ \text{CH}\cdot\text{CO}\cdot\text{C}\cdot\text{COMe}\end{array} +$$

$$\left[\text{CH}_2(\text{NO}_2)\cdot\text{CO}_2\text{H}\right] \quad \begin{array}{l}\text{CH}_2\cdot\text{OH} \\ \text{CO}_2\text{H}\end{array} + \text{HNO}_2.$$

Reaction between Triacetic Lactone and Ethyl-β-aminocrotonate.

Triacetic lactone reacts with ethyl β-aminocrotonate in presence of sulphuric acid, alcoholic hydrochloric acid, or glacial acetic acid to give in each case the pyrone lactone already described, and, in the latter case, a second substance containing nitrogen. The effect of all three reagents was examined. When hydrochloric acid was used under similar conditions to those of the previous experiment a very small yield was always obtained, with sulphuric acid the yield was much increased, but the best results were given by the use of glacial acetic acid as follows:

6·2 grams of triacetic lactone, 7·5 grams of ethyl β-aminocrotonate, and 25 c.c. of glacial acetic acid were heated almost to boiling and left to cool. A mass of fine needles separated which were found to consist of nearly pure pyrone lactone. 3·1 grams were obtained, corresponding to a yield of 32·5 per cent.

The mother liquor was poured into 70 c.c. of water, quickly filtered from a small quantity of impure pyrone lactone which separated, diluted with 100 c.c. of water, and left to stand. A granular crystalline precipitate slowly formed, which after twenty-four hours' standing was collected, washed with a little water, and dried in a vacuum. 2·5 grams were obtained.

The substance was recrystallised from a mixture of methyl alcohol and water (1 : 4), from which it separated in colourless granular crystals melting indefinitely, from about 180° to about 200°.

A considerable quantity of the substance was prepared by this method.

Attempts to purify it by recrystallisation and fractionation failed, no substance of definite melting point being obtained, whilst at the same time each sample was proved to contain a small amount of the pyrone lactone, since it gave the same blue fluorescence when dissolved in strong sulphuric acid. The substance was therefore treated with a small quantity of alcoholic potash.

Two grams of the substance dissolved in a little alcohol were heated on the water-bath for fifteen minutes with 10 c.c. of a 10 per cent. solution of alcoholic potash. The solution was then poured into 100 c.c. of water acidified with hydrochloric acid and left to stand overnight. A white, crystalline solid separated which, after being dried in a vacuum, amounted to 1·1 grams. On recrystallisation from methyl alcohol the substance separated in flat plates melting at 193°, and which no longer showed fluorescence when dissolved in strong sulphuric acid. The pyrone lactone originally present had therefore been destroyed.

After a second recrystallisation:

0·2391 gave 0·5210 CO_2 and 0·1319 H_2O. C = 59·42; H = 6·13.

0·2684 ,, 10·3 c.c. moist nitrogen at 11·0° and 759 mm. N = 4·57.

$C_{16}H_{12}O_6N$ requires C = 59·81. H = 5·91; N = 4·36 per cent.

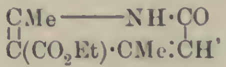
The substance is insoluble in water, light petroleum, or ether readily soluble in hot alcohol, methyl alcohol, or chloroform, and slightly so in ethyl acetate or benzene. It dissolves in dilute aqueous sodium hydroxide without giving a coloured solution, and if boiled for some time with very concentrated alkali, ammonia is evolved.

With ferric chloride in alcoholic solution no coloration is produced. The mother liquor from the preparation of this substance was rendered faintly acid and evaporated to a very small bulk, when an oily substance separated which quickly solidified on cooling. On addition of hydrochloric acid the greater part dissolved, leaving a very small quantity of a brown residue, which was filtered off and the solution made nearly neutral. On standing for some time a white, feathery solid separated which was collected, washed with a little water and dried in a vacuum. This substance, which contained nitrogen, melted at 138°; yield 0·2 gram.

In order to ascertain whether it was present in the original impure substance, a series of experiments were made in which the quantity of alcoholic potash and time of boiling were increased. In each case a greater quantity of the substance was formed, thus showing that it was a decomposition product.

Reaction between Alcoholic Potash and the Substance $C_{16}H_{19}O_6N$.—Two grams of the compound $C_{16}H_{19}O_6N$ were boiled for one hour with 30 c.c. of alcoholic potash of the same strength as before, poured into 150 c.c. of water, acidified and left to stand when 0·6 gram of the original substance $C_{16}H_{19}O_6N$ separated, and, after evaporation as before, 0·83 gram of the second substance was obtained. This was mixed with the former preparations and the whole crystallised from hot water, being obtained in fine needles, which slowly changed to granular crystals on standing.

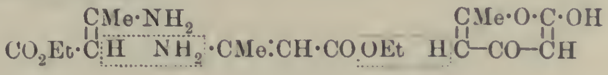
The substance melted at 138° and proved to be identical with the ethyl ester of ψ-lutidostyrilcarboxylic acid, corresponding to the formula



$$\begin{array}{l}\mathrm{CMe{-\!-\!-}NH\cdot CO}\\ \mathrm{C(CO_2Et)\cdot CMe{:}CH}\end{array},$$

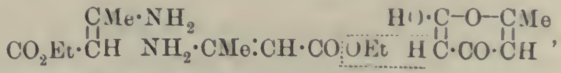
previously obtained by the action of pure, dry hydrogen chloride on β-aminocrotonic ester at 120° (Collie, Trans., 1897, 71, 303), and by the action of ammonia on the ethyl ester of *iso*dehydracetic acid at 150—160° (Anschütz, Bendix, and Kerp, *Annalen*, 1890, **259**, 173), for on treatment with strong aqueous alkali for some time, it yielded the corresponding acid melting at 295° (given as 304° approx. in the literature).

The production of this ester makes it evident that in the formation of the substance $C_{16}H_{19}O_6N$ two molecules of ethyl β-aminocrotonate had taken part, thus:



$$\begin{array}{l}\mathrm{\quad\quad\quad\;\; CMe\cdot NH_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CMe\cdot O\cdot C\cdot OH}\\ \mathrm{CO_2Et\cdot C\boxed{H\quad NH_2}\cdot CMe{:}CH\cdot CO\boxed{OEt\quad H}C{-}CO{-}CH}\end{array}$$

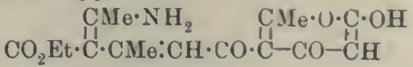
or



$$\begin{array}{l}\mathrm{\quad\quad\quad\;\; CMe\cdot NH_2 \qquad\qquad\qquad\qquad\qquad\qquad\quad HO\cdot C{-}O{-}CMe}\\ \mathrm{CO_2Et\cdot CH\quad NH_2\cdot CMe{:}CH\cdot CO\boxed{OEt\quad H}C\cdot CO\cdot CH}\end{array},$$

giving a compound of the type

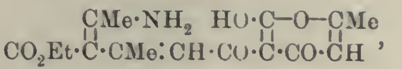
(1)



$$\begin{array}{l}\mathrm{\quad\quad\quad\;\; CMe\cdot NH_2 \qquad\qquad\quad CMe\cdot O\cdot C\cdot OH}\\ \mathrm{CO_2Et\cdot C\cdot CMe{:}CH\cdot CO\cdot C{-}CO{-}CH}\end{array}$$

or of the type

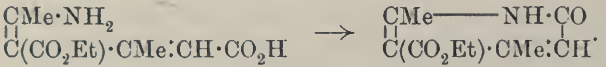
(2)



$$\begin{array}{l}\mathrm{\quad\quad\quad\;\; CMe\cdot NH_2\quad HO\cdot C{-}O{-}CMe}\\ \mathrm{CO_2Et\cdot C\cdot CMe{:}CH\cdot CO\cdot C\cdot CO\cdot CH}\end{array},$$

of which the latter is the more probable, since the lactone is produced at the same time.

The lactone ring is then separated under the influence of alcoholic potash and a free acid is obtained which at once yields the lutidone ester with loss of water:



$$\begin{array}{l}\mathrm{CMe\cdot NH_2}\\ \|\\ \mathrm{C(CO_2Et)\cdot CMe{:}CH\cdot CO_2H}\end{array} \longrightarrow \begin{array}{l}\mathrm{CMe}\text{——}\mathrm{NH\cdot CO}\\ \|\qquad\qquad\quad |\\ \mathrm{C(CO_2Et)\cdot CMe{:}CH}\end{array}$$

The last reaction is practically quantitative. In the above experiment, out of 2 grams of the original substance $C_{16}H_{19}O_6N$, 0·6 gram was recovered unchanged, and the remaining 1·4 grams gave 0·83 gram of the lutidone ester, corresponding to a yield of 97 per cent.

That the substance $C_{16}H_{19}O_6N$ is not merely a molecular compound of triacetic lactone and the lutidone ester is proved by the fact that, if a solution of the two is evaporated to dryness and the product very carefully fused, the lutidone remains unchanged, whilst the lactone is partly decomposed.

In conclusion, the author desires to express his best thanks to Professor Collie, at whose suggestion the research was undertaken, and who has given him every help throughout the work.

The Organic Chemistry Laboratory,
University College,
London.

XXV.—*Oxidation of Hydrocarbons of the Benzene Series.*

By Herbert Drake Law and Frederick Mollwo Perkin.

In recent papers we have shown (*Trans. Faraday Soc.*, 1905, 1, 31, 251) that by the electrolytic oxidation of toluene, the three xylenes, ethylbenzene, mesitylene, cumene, and ψ-cumene in acid solution aldehydes were formed. In the case of toluene and *m*-xylene in alkaline solution, the hydrocarbons were oxidised to carbon dioxide and water.

In the present paper we describe experiments made on the oxidation of these hydrocarbons by purely chemical methods in which the reagents employed were lead peroxide, manganese peroxide, chromyl dichloride, and persulphates. In the latter case oxidising action was accelerated by the addition of a silver salt as catalytic agent, because, in the absence of such a catalyst, practically no oxidation takes place.

Lead Peroxide.—When a mixture of toluene or other hydrocarbon of the benzene series and 50 per cent. sulphuric acid is treated with lead peroxide according to the equation

$$R{\cdot}CH_3 + 2PbO_2 + 2H_2SO_4 = R{\cdot}CHO + 2PbSO_4 + 2H_2O,$$

a very energetic reaction takes place, and unless the lead peroxide is very slowly added or the mixture very thoroughly cooled, the oxidation is so vigorous that the mixture boils over. We found that by this method the hydrocarbons toluene, the xylenes, mesitylene, ψ-cumene, and cymene all gave varying quantities of the mono-aldehydes.

In the first experiments freshly precipitated lead peroxide was employed, but it was not found to be any more reactive than the ordinary commercial product.

Manganese Peroxide.—Fournier (*Compt. rend.*, 1901, **133**, 634) studied the action of manganese peroxide in presence of sulphuric acid of sp. gr. 1·53 on hydrocarbons of the benzene series, and found that aldehydes were produced; *o*-xylene, for example, yielded about 30 per cent. of *o*-tolualdehyde. We have repeated Fournier's experiments, and in most cases obtained results corresponding very closely to those described by him.

Chromyl Dichloride.—Étard (*Ann. Chim. Phys.*, 1881, [v], **22**, 218) and Bornemann (*Ber.*, 1884, **17**, 1463) have shown that when chromyl dichloride acts on hydrocarbons of the benzene series an additive compound of the hydrocarbon and the chromyl dichloride is produced, in which two molecules of the chromyl dichloride unite with one molecule of the hydrocarbon:

$$R{\cdot}CH_3 + 2CrO_2Cl_2 = R{\cdot}CH(OH{\cdot}CrOCl_2)_2.$$

This substance is decomposed by water with production of an aldehyde:

$$3R{\cdot}CH(OH{\cdot}CrOCl_2) + Aq = 3R{\cdot}CHO + 4CrCl_3 + 2CrO_3 + Aq.$$

In the majority of cases we have obtained better yields of aldehydes by this method than by any other which we have tried. Owing to the vigour of the reaction, however, special precautions must be employed.

*Persulphates.**—When toluene is agitated with a mixture of ammonium persulphate and 4*N*-sulphuric acid, no oxidation takes place. Now, although persulphuric acid alone does not oxidise hydrocarbons of the benzene series, it occurred to us that if a metallic salt were present oxidation might take place. Marshall (*Proc. Roy. Soc. Edin.*, 1900, **23**, 163) and Marshall and Inglis (*Proc. Roy. Soc. Edin.*, 1902, **24**, 88) have shown that when a persulphate is acted on by a soluble silver salt, a black precipitate of silver peroxide is formed. This is probably due to the hydrolysis of the silver persulphate first produced.* When ammonium persulphate is employed, a portion of the ammonium residue is oxidised to nitric acid, $8(NH_4)_2S_2O_8 + 6H_2O = 7(NH_4)_2SO_4 + 9H_2SO_4 + 2HNO_3$.

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* Since we commenced this work, our attention has been directed to the work of R. Kempf (*Ber.*, 1905, **38**, 3963; 1906, **39**, 3715), who has investigated the action of persulphates in presence of a silver salt on benzene and *p*-benzoquinone. He has, however, allowed the oxidation to proceed to the furthest possible limit, whilst we have been chiefly concerned with the preparation of the aldehydes.

This mixture will bleach indigo and oxidise chromic salts. We find that when toluene or other benzene hydrocarbons are agitated with a mixture of a persulphate in sulphuric acid and a small quantity of a silver salt that oxidation takes place and that an aldehyde is the first product. If the alcohol is formed, we have not so far succeeded in isolating it.

At first sodium persulphate was employed, but the results were very contradictory. With some specimens the oxidation was very complete; with others there was practically no action. We found that when oxidation did not take place the persulphate was always contaminated with chloride; therefore in all the later experiments ammonium persulphate free from chloride was used.

The persulphate reaction is rather difficult to control, and the results in various experiments with the same hydrocarbon under apparently similar conditions were not very concordant.

EXPERIMENTAL.

Oxidation of Toluene.

I. *With Lead Peroxide.*—Two hundred and eighty grams of lead peroxide (theory requires 260) was mixed in a lead vessel, surrounded by ice, with 300 c.c. of sulphuric acid (equal volumes of concentrated acid and water, sp. gr. 1·52). The top of the vessel was closed with a sheet of lead, through which a lead stirrer was passed and a tube connected with a carbon dioxide generator, so that the operation could be carried out in an atmosphere of the gas. The mixture was vigorously agitated until the temperature had fallen to about 2°. Then 50 grams of toluene were added and the agitation continued. The temperature rapidly rose to 40°, but soon fell again and remained between 10° and 15° during three hours, when the agitation was stopped. The mixture, which had a strong odour of benzaldehyde, was now transferred to a round-bottomed flask and heated on the water-bath for about half an hour, when it was distilled in a current of steam. We found it always desirable to heat the mixture in this way before subjecting it to steam distillation in order that the reaction might be completed. When this was not done there was a tendency for the mixture to froth over when steam was passed into it.

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* The oxidation is probably brought about by the unstable silver peroxide, and is not directly due to the persulphuric acid. It will, however, proceed as long as there is any persulphuric acid present, because as soon as the silver peroxide has parted with its oxygen, it will react with the persulphuric acid and thus silver peroxide will again be formed.

The distillate was extracted with ether and the aldehyde converted into the hydrogen sulphite compound, in order to separate it from any unchanged toluene. On decomposing the hydrogen sulphite compound 24 per cent. of benzaldehyde was obtained.

When ice was not used and the toluene was added in small quantities at a time, taking care not to allow the temperature to rise above 35 to 40°, we never obtained more than about 18 per cent. of benzaldehyde.

II. *Manganese Peroxide.*—One hundred grams of commercial manganese peroxide (theory requires 83 grams MnO_2) were mixed in a lead vessel with 300 c.c. of sulphuric acid, sp. gr. 1·52, and then 50 grams of toluene added. The mixture was vigorously agitated for five hours. After heating on the water-bath and distilling with steam, only 0·5 per cent. of benzaldehyde was obtained.

The experiment was then repeated, taking, however, 100 grams of freshly precipitated manganese peroxide and agitating for 6·5 hours. In this case 5 per cent. of benzaldehyde was obtained.

III. *Chromyl Dichloride.*—One hundred and forty grams of chromyl dichloride were dissolved in 200 c.c. of chloroform and placed in a glass jar fitted with a glass stirrer, and surrounded by cold water. Forty grams of toluene were dissolved in twice its volume of chloroform and allowed to run slowly into the well-agitated solution of chromyl dichloride. When the whole of the toluene had been added, the mixture was agitated for half an hour longer (altogether two hours) and allowed to stand overnight. It was then transferred to a round-bottomed flask containing a little water, and sulphurous acid was carefully added in excess. During the addition of the sulphurous acid, the flask and its contents were gently agitated. The mixture was distilled with steam, the chloroform containing the dissolved aldehyde separated from the water, and the chloroform evaporated. The oily product was shaken with a concentrated solution of sodium hydrogen sulphite. The hydrogen sulphite compound was washed with ether to free it from any unchanged toluene and the aldehyde recovered in the usual manner. Yield of benzaldehyde, 44 per cent.

IV. *Persulphates.*—Two hundred grams of ammonium persulphate were mixed with 500 c.c. of 4*N*-sulphuric acid, and 2 grams of silver sulphate and 40 grams of toluene added. The top of the vessel was closed with a sheet of lead, through which passed a glass stirrer and a tube in connexion with a Kipp's apparatus for generating carbon dioxide. The mixture was vigorously agitated without cooling, so as to form an emulsion. The temperature rose to 45°; after seven hours, it had fallen to that of the atmosphere and the mixture was distilled with steam. The benzaldehyde was separated as usual by means of the hydrogen sulphite compound, the yield being 78 per cent.

With $2N$-acid, the yield of aldehyde was poor.

p-*Xylene.*

Lead Peroxide.—Fifty grams of *p*-xylene were added to 300 c.c. of sulphuric acid, sp. gr. 1·52, and the mixture thoroughly agitated in an atmosphere of carbon dioxide. Two hundred and fifty grams of lead peroxide were then added in quantities of about 50 grams at one time, by which means the temperature of the mixture was kept at about 45°. The whole operation took about three hours. The mixture was then transferred to a flask and heated on the water-bath for about half an hour, after which it was distilled with steam. The yield of aldehyde was 27·5 per cent.

Manganese Peroxide.—Fifty grams of *p*-xylene were mixed so as to form an emulsion with 100 grams of manganese peroxide and 300 c.c. of sulphuric acid, sp. gr. 1·52. The mixing was continued for about six hours, during which time the temperature did not rise above 25°. The mixture was then heated on the water-bath for half an hour and distilled with steam. The yield of aldehyde was 14·5 per cent.

Chromyl Dichloride.—The preparation was exactly similar to that described under toluene, and the yield of aldehyde varied between 70 and 80 per cent.

Persulphate.—In this case, it was found essential to cool the mixture during the time the reaction was taking place. In one case, taking 40 grams of *p*-xylene, 190 grams of ammonium persulphate, 500 c.c. of $4N$-sulphuric acid, and 2 grams of silver sulphate, the temperature at the commencement was 15°; in fifty minutes it had risen to 29°, and ten minutes later the mixture boiled over, the temperature having risen to 102°. When the above mixture was well agitated in an atmosphere of carbon dioxide, the vessel being placed in cold water so that the temperature did not rise above 25°, yields of *p*-tolualdehyde varying from 35 to 48 per cent. were obtained.

The methods of procedure with *o*- and *m*-xylene were similar to those employed for *p*-xylene; the yields obtained by the different processes of oxidation are tabulated on page 263. Mesitylene and ψ-cumene also behaved in a normal manner, but the yields of aldehyde were less than in the cases of the xylenes.

Cymene was found to be very difficult to oxidise, even when the temperature, in the case of oxidation with lead peroxide, manganese peroxide, and persulphates, was allowed to rise unchecked. This was from 40 to 50° in the case of the peroxides, using acid of sp. gr. 1·53. With persulphates the temperature, using $4N$-acid, rose to about 35°. In this case the reaction showed a tendency to proceed beyond the aldehyde stage and a considerable quantity of cuminic acid was obtained, the yield of cuminaldehyde being very small. The aldehyde is probably first produced and then undergoes oxidation, for a considerable amount of unchanged cymene was always recovered.

Although the main product of oxidation of all the hydrocarbons was the mono-aldehyde, on working up the residues from a large number of experiments small quantities of the alcohols were obtained. The amounts, however, were so small that they certainly did not represent more than 0·1 per cent. of the hydrocarbon employed. At the same time the fact that these small quantities of alcohols are obtained would point to the probability that the alcohol is the first product, and that by further oxidation the aldehyde is formed. In some cases a considerable quantity of resin was produced, and this was particularly marked when persulphates were employed.

Percentage yield of aldehydes with different oxidising agents.

	Electrolytic oxidation.	Lead peroxide.	Manganese peroxide.	Persulphates.	Chromyl dichloride.
Toluene	10—20	18—24	5	78	44
o-Xylene	25—30	28	38	—	65
p-Xylene..	25—35	27·5	14·5	35—48	70—80
m-Xylene	10—15	20	—	44	60
Mesitylene	10—15	8·5	16	5·8	5·5
ψ-Cumene	10—12	11	17	—	5
Cymene	10, aldehyde 20, alcohols	10	1	0·5	8

It should also be mentioned that when the hydrocarbons were oxidised with chromyl dichloride, in some cases considerable quantities of chlorinated products were obtained. This was usually the case when the yield of aldehyde was small and was particularly noticeable with mesitylene and *m*-xylene.

The authors desire to express their thanks to the Committee of the Government Research Fund of the Royal Society for a grant which, in part, defrayed the expenses in connexion with this investigation.

Chemical Laboratory,
Borough Polytechnic Institute,
Borough Road, London.

XXVI.—*The Condensation of Salicylamide with Aryl Aldehydes.*

By CHARLES ALEXANDER KEANE and WILLIAM WALTER SCOTT NICHOLLS.

THE condensation of amides with aldehydes was first studied by Roth (*Annalen*, 1870, **154**, 72), who attempted to prepare the amide of cinnamic acid by heating acetamide with benzaldehyde. The product he obtained was shown to be benzylidenediacetamide,

$$C_6H_5\cdot CH(NH\cdot CO\cdot CH_3)_2,$$

and many similar compounds have since been prepared by the condensation of both aryl and alphyl aldehydes with the amides of monobasic acids by Schuster (*Annalen*, 1870, **154**, 80), Nencki (*Ber.*, 1874, **7**, 158), Hofmann and Meyer (*Ber.*, 1892, **25**, 209), Pulvermacher (*Ber.*, 1892, **25**, 311), and Bülow (*Ber.*, 1893, **26**, 1972).

These condensation products are formed by the action of two molecules of the amide on one of the aldehyde, according to the equation:

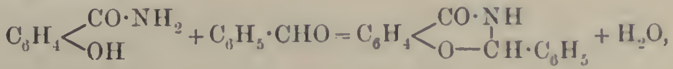
$$R\cdot CH{:}\,\vdots\, O + \begin{matrix} H\cdot\vdots NH\cdot CO\cdot R' \\ H\cdot\vdots NH\cdot CO\cdot R \end{matrix} = R\cdot CH{<}\begin{matrix} NH\cdot CO\cdot R' \\ NH\cdot CO\cdot R' \end{matrix} + H_2O.$$

Compounds of a different type are obtained by the condensation of formaldehyde with amides (Einhorn, *Annalen*, 1905, **343**, 207), when one molecule of the amide and one of the aldehyde interact to form *N*-methylol compounds, $R\cdot CO\cdot NH\cdot CH_2\cdot OH$, from which methylene compounds of analogous constitution to the above, $CH_2{:}(NH\cdot CO\cdot R)_2$, can be prepared in several instances by the further action of amides.

These substances show varying degrees of stability towards dilute acids and dilute alkalis, a property which is of special interest in connexion with the physiological action of the amides, and it is from this consideration that the action of aldehydes on salicylamide has been studied.

Salicylamide, when heated with benzaldehyde, either with or without a solvent, in presence of hydrochloric acid or of sodium acetate, condenses to form a well-defined compound in the production of which one molecule of the amide reacts with one of the aldehyde. The substance gives no reaction with ferric chloride, indicating that the hydroxyl group of the salicylamide has participated in the condensation and it yields an acetyl derivative which is decomposed by concentrated sulphuric acid with the formation of *N*-acetylsalicylamide (McConnan and Titherley, Trans., 1906, **89**, 1318) and benzaldehyde.

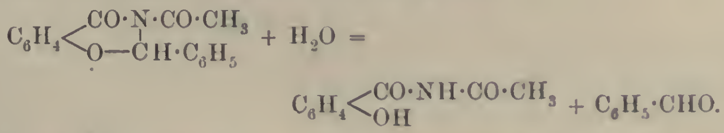
Hence it is concluded that the condensation takes place according to the equation:



$$C_6H_4<\begin{array}{l}CO\cdot NH_2\\ OH\end{array} + C_6H_5\cdot CHO = C_6H_4<\begin{array}{l}CO\cdot NH\\ O-CH\cdot C_6H_5\end{array} + H_2O,$$

with the formation of a cyclic compound of the oxazine group, namely, 2-phenyl-1 : 3-benzoxazone. An alternative tautomeric structure is, of course, also possible.

The decomposition of the acetyl derivative into *N*-acetylsalicylamide and benzaldehyde, which indicates the presence of the iminogroup in the ring, is represented by the equation:



$$C_6H_4<\begin{array}{l}CO\cdot N\cdot CO\cdot CH_3\\ O-CH\cdot C_6H_5\end{array} + H_2O =$$
$$C_6H_4<\begin{array}{l}CO\cdot NH\cdot CO\cdot CH_3\\ OH\end{array} + C_6H_5\cdot CHO.$$

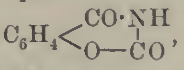
Anisaldehyde behaves similarly to benzaldehyde, and the condensation product also yields an acetyl derivative, whilst *o*-methoxybenzamide, in which the hydrogen of the hydroxyl group is substituted, forms the ordinary benzylidene condensation product,

$$C_6H_5\cdot CH\colon(HN\cdot CO\cdot C_6H_4\cdot O\cdot CH_3)_2,$$

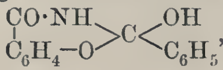
benzylidenebis-*o*-methoxybenzamide; this is not acetylated by heating with acetic anhydride.

Both dilute alkalis and dilute acids regenerate salicylamide and benzaldehyde or anisaldehyde from 2-phenyl-1 : 3-benzoxazone or from the corresponding anisaldehyde compound; they are also decomposed by heating with bases such as aniline or piperidine. From a direct comparison with the condensation products of the type of benzylidenedibenzamide, the above cyclic compounds are less stable towards alkalis and about equally stable towards dilute mineral acids. They are further distinguished by being acetylated by the action of acetic anhydride, whereas the benzylidene compounds are either decomposed or are unacted on; benzylidenediacetamide and benzylidenedibenzamide are, for example, decomposed, whilst benzylidenebis-*o*-methoxybenzamide is not attacked.

The above oxazone ring is present in carbonylsalicylamide,



$$C_6H_4<\begin{array}{l}CO\cdot NH\\ O-CO\end{array},$$

described by Einhorn and Mettler (*Ber.*, 1902, **35**, 3647), and by Einhorn and Schmidlin (*Ber.*, 1902, **35**, 3653), and also in the closed chain formula suggested by McConnan and Titherley (Trans., 1906, 89, 1318) as representing the structure of one of the tautomeric forms of benzoylsalicylamide,  $\begin{matrix}\mathrm{CO\cdot NH}\\ |\\ \mathrm{C_6H_4{-}O}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{OH}\\ \mathrm{C_6H_5}\end{matrix}$, and of other acyl salicylamides.*

Condensation products of other hydroxyamides with aldehydes have been prepared directly from mandelamide and benzaldehyde by Michael and Jeanpêtre (*Ber.*, 1892, **25**, 1678), and indirectly from mandelonitrile, lactonitrile, and anisonitrile by E. Fischer (*Ber.*, 1896, **29**, 205) and by Minovici (*Ber.*, 1896, **29**, 2097).

In each case the condensation takes place between one molecule of the amide or nitrile and one molecule of the aldehyde, and the products have been regarded as having the general formula

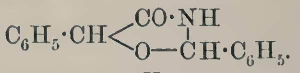
$$\mathrm{R\cdot CH(OH)\cdot CO\cdot N{:}CH\cdot R'},$$

and therefore analogous in structure to the condensation products of aldehydes with primary amines.

Michael and Jeanpêtre (*loc. cit.*), in discussing the following alternative formula for the condensation product of mandelamide and benzaldehyde, regard formula I as correct, because it forms an acetyl compound and is not acted on by nitrous acid.

$$\mathrm{C_6H_5\cdot CH(OH)\cdot CO\cdot N{:}CH\cdot C_6H_5}$$

I.



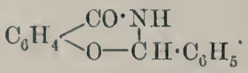
$$\mathrm{C_6H_5\cdot CH}\!<\!\begin{matrix}\mathrm{CO\cdot NH}\\ \quad\;|\\ \mathrm{O{-}CH\cdot C_6H_5}\end{matrix}.$$

II.

By analogy with the salicylamide condensation product the formula II would, on the contrary, appear the more probable.

This point is under investigation, as is also the condensation of salicylamide with other aldehydes and of other hydroxyamides with aldehydes, including the aldoses.

EXPERIMENTAL.

2-Phenyl-1 : 3-*benzoxazone*,  $\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{CO\cdot NH}\\ \quad\;|\\ \mathrm{O{-}CH\cdot C_6H_5}\end{matrix}$.

The condensation of salicylamide with benzaldehyde is effected by melting together one molecular proportion of the amide with one and a half molecular proportions of the aldehyde on the water-bath; when the whole forms a homogeneous liquid, a few drops of concentrated hydrochloric acid are added and the heating continued for five to six hours. The product of the reaction is washed with a little ether to remove the excess of benzaldehyde, and then macerated with very dilute sodium hydroxide solution for a few minutes to remove the unchanged salicylamide. The residual condensation product is purified by crystallisation from alcohol and is thus obtained quite free from salicylamide. Fractional crystallisation from chloroform can be substituted for the treatment with alkali as salicylamide is considerably less soluble than the oxazone in this solvent. Dry sodium acetate can be used in place of hydrochloric acid as the condensing agent, and the condensation can also be effected in alcoholic or in chloroform solution.

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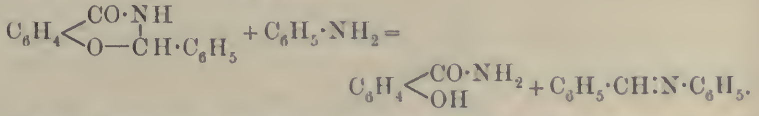
* Dr. A. W. Titherley, who has also prepared phenylbenzoxazone, is studying its relation to the cyclic tautomerism of the acyl salicylamides. (Private communication.)

Phenylbenzoxazone crystallises in silky needles which melt at 169°; it dissolves fairly readily in ether or chloroform, very readily in hot alcohol or hot benzene. It gives no coloration with ferric chloride:

0·1818 gave 0·4988 CO_2 and 0·0802 H_2O. C = 74·82; H = 4·91.
0·1862 ,, 10·7 c.c. moist nitrogen at 28° and 766 mm. N = 6·36.
0·5064 in 20 c.c. alcohol gave Δt – 0·20. M.W. = 197·5.
$C_{14}H_{11}O_2N$ requires C = 74·67; H = 4·89; N = 6·22 per cent.; M.W = 225.

It is insoluble in cold water, but is gradually decomposed into benzaldehyde and salicylamide on prolonged boiling. Treated with cold sodium hydroxide solution, complete decomposition is effected on standing; it is stable towards cold dilute mineral acids, but decomposition readily takes place on warming. Heated with aniline, complete decomposition into benzylideneaniline (m. p. 54°) and salicylamide occurs according to the equation:

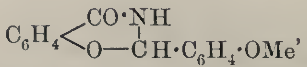


$$C_6H_4<\begin{matrix}CO\cdot NH\\ O-\overset{|}{C}H\cdot C_6H_5\end{matrix} + C_6H_5\cdot NH_2 = C_6H_4<\begin{matrix}CO\cdot NH_2\\ OH\end{matrix} + C_6H_5\cdot CH{:}N\cdot C_6H_5.$$

1-*Acetyl*-2-*phenyl*-1 : 3-*benzoxazone* is prepared by heating the above substance with acetic anhydride. It crystallises from alcohol in thin prisms which melts at 88°; it is slightly soluble in boiling water and readily so in cold benzene:

0·2538 gave 12·3 c.c. moist nitrogen at 22° and 764 mm. N = 5·52.
$C_{16}H_{13}O_3N$ requires N = 5·24 per cent.

It is decomposed into its constituents by heating with dilute alkali or with dilute mineral acids. When dissolved in concentrated sulphuric acid and poured into water, *N*-acetylsalicylamide and benzaldehyde are formed. The identity of the former product was checked by comparison with a specimen of *N*-acetylsalicylamide kindly placed at our disposal by Dr. Titherley; both melted at the same temperature (146°) and showed no depression of the melting point on being mixed together. When heated with aniline, decomposition takes place with the formation of benzylideneaniline, acetanilide, and salicylamide. The acetyl compound, like the parent substance, gives no coloration with ferric chloride.

2-p-*Methoxyphenyl*-1 : 3-*benzoxazone*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO\cdot NH}{O-\overset{|}{C}H\cdot C_6H_4\cdot OMe}$, is prepared from anisaldehyde and salicylamide similarly to the phenyl compound, and is in every respect analogous to the latter. It crystallises from alcohol in fine prisms, which melt at 166—167°; it is slightly soluble in cold alcohol or cold benzene, readily so in chloroform, hot alcohol, or hot benzene :

0·1891 gave 8·7 c.c. moist nitrogen at 15° and 762 mm. N = 5·40.
$C_{15}H_{13}O_3N$ requires N = 5·49 per cent.

The *acetyl* derivative resembles the corresponding phenyl compound in all its properties. It crystallises from alcohol in well-defined prisms which melt at 91°:

0·3928 gave 16·4 c.c. moist nitrogen at 11° and 770 mm. N = 5·04.
$C_{17}H_{15}O_4N$ requires N = 4·72 per cent.

Benzylidenebis-o-methoxybenzamide, $C_6H_5\cdot CH{:}(NH\cdot CO\cdot C_6H_4\cdot OMe)_2$.

This compound was prepared chiefly to compare its properties with those of the cyclic condensation products. It is obtained in a similar manner by the action of two molecular proportions of the amide on one and a half molecular proportions of the aldehyde, in presence of hydrochloric acid as the condensing agent.

It crystallises in fine needles which melt at 156°; it is slightly soluble in cold alcohol or cold benzene, readily so in both solvents on heating, and is also readily soluble in chloroform :

0·3032 gave 19·7 c.c. moist nitrogen at 20° and 754 mm. N = 7·37.
$C_{23}H_{22}O_4N_2$ requires N = 7·18 per cent.

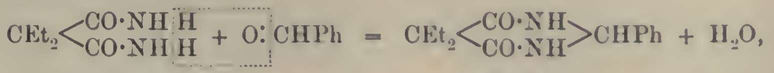
This benzylidene compound is much more stable towards alkalis than the oxazones, being only decomposed into its constituents by boiling with a concentrated solution of alkali hydroxide ; it is also somewhat more stable towards dilute mineral acids. Heated with acetic anhydride, it is neither acetylated nor decomposed, the unchanged product (m. p. 156°) being recovered.

CHEMISTRY DEPARTMENT,
THE SIR JOHN CASS TECHNICAL INSTITUTE,
ALDGATE.

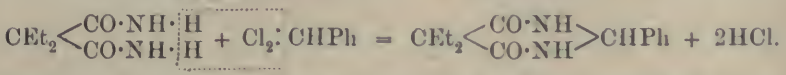
XXVII.—*The Condensation of Diethylmalonamide with Aldehydes.*

By HARRY BURROWS and CHARLES ALEXANDER KEANE.

DIETHYLMALONAMIDE, when heated with benzaldehyde in presence of hydrochloric acid, condenses to form a compound in which one molecular proportion of the amide reacts with one of the aldehyde, as in the condensation of salicylamide with benzaldehyde (compare Keane and Nicholls, preceding paper). The same compound is formed by heating diethylmalonamide with benzylidene chloride. The condensation is therefore regarded as taking place according to the following equations :



$$\mathrm{CEt_2}<\begin{matrix}\mathrm{CO\cdot NH\,H}\\ \mathrm{CO\cdot NH\,H}\end{matrix} + \mathrm{O\!:\!CHPh} = \mathrm{CEt_2}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CHPh} + \mathrm{H_2O},$$



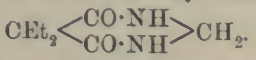
$$\mathrm{CEt_2}<\begin{matrix}\mathrm{CO\cdot NH\cdot H}\\ \mathrm{CO\cdot NH\cdot H}\end{matrix} + \mathrm{Cl_2\!:\!CHPh} = \mathrm{CEt_2}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CHPh} + 2\mathrm{HCl}.$$

with the formation of a cyclic compound of the pyrimidine group, 4 : 6-diketo-2-phenyl-5 : 5-diethylhexahydropyrimidine. Cinnamaldehyde reacts similarly. Both compounds form diacetyl derivatives on heating with acetic anhydride ; they are stable towards dilute mineral acids, but are gradually decomposed when heated with dilute alkali.

This condensation differs from that of diethylmalonamide with formaldehyde (Einhorn, *Annalen*, 1905, **343**, 272) which yields only the open chain compound *N*-dimethyloldiethylmalonamide,

$$\mathrm{CEt_2(CO\cdot NH\cdot CH_2\cdot OH)_2},$$

and not the closed chain derivative methylenediethylmalonamide,



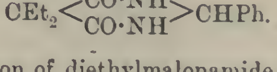
$$\mathrm{CEt_2}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CH_2}.$$

Chloral also reacts with diethylmalonamide, but forms an addition compound only, not a condensation product.

The application of this reaction to the condensation of diethylmalonamide with other aldehydes and to that of aldehydes with the amides of other dibasic acids is under investigation.

EXPERIMENTAL.

4 : 6-*Diketo-2-phenyl-5 : 5-diethylhexahydropyrimidine*,



$$\mathrm{CEt_2}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CHPh}.$$

One molecular proportion of diethylmalonamide and a little more than one molecular proportion of benzaldehyde together with a few drops of concentrated hydrochloric acid are heated on the oil-bath to 150° for about two hours, when the whole becomes solid. The product is washed with ether to remove the excess of benzaldehyde and the residue purified by crystallisation from alcohol. The condensation can also be carried out in alcoholic solution.

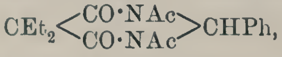
The preparation from benzylidene chloride and diethylmalonamide is effected by heating molecular proportions of the two substances together until the evolution of hydrochloric acid ceases.

The condensation product crystallises from alcohol in prisms which melt at 262°. It is sparingly soluble in all the ordinary solvents, insoluble in light petroleum, and moderately soluble in hot alcohol:

0·2042 gave 0·5106 CO_2 and 0·1372 H_2O. C = 68·19; H = 7·46.
0·2436 ,, 23·4 c.c. moist nitrogen at 11° and 771 mm. N = 11·61.
$C_{14}H_{18}O_2N_2$ requires C = 68·29; H = 7·31; N = 11·38 per cent.

It is not altered when boiled with dilute hydrochloric acid, but is gradually decomposed into its constituents when boiled with dilute sodium hydroxide solution.

4 : 6-*Diketo*-1 : 3-*diacetyl*-2-*phenyl*-5 : 5-*diethylhexahydropyrimidine*,



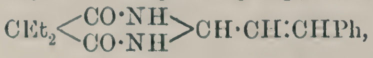
$$CEt_2{<}{\begin{matrix}CO\cdot NAc\\ CO\cdot NAc\end{matrix}}{>}CHPh,$$

is prepared by heating the above compound with excess of acetic anhydride. It crystallises from light petroleum in prisms which melt at 147°; it is readily soluble in chloroform, benzene, or hot alcohol:

0·3662 gave 27·3 c.c. moist nitrogen at 14° and 765 mm. N = 8·81.
$C_{18}H_{22}O_4N_2$ requires N = 8·48 per cent.

When treated with cold concentrated sulphuric acid, the acetyl groups are removed and the original pyrimidine regenerated (m. p. 262°).

4 : 6-*Diketo-2-cinnamyl*-5 : 5-*diethylhexahydropyrimidine*,



$$CEt_2{<}{\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}}{>}CH\cdot CH{:}CHPh,$$

is prepared similarly to the phenyl compound. It crystallises from alcohol in needles which melt at 241°; it is readily soluble in hot alcohol, acetone, or chloroform, sparingly so in ether, and fairly soluble in hot benzene or hot ethyl acetate:

0·1986 gave 0·5108 CO_2 and 0·1392 H_2O. C = 70·15; H = 7·78.
0·4888 ,, 44·5 c.c. moist nitrogen at 16° and 761 mm. N = 10·64.
$C_{16}H_{20}O_2N_2$ requires C = 70·58; H = 7·35; N = 10·29 per cent.

The divergence of the above data from the theoretical values is due to the difficulty of removing the last traces of diethylmalonamide from the condensation product.

The cinnamyl compound resembles the phenyl compound in its behaviour towards acids and alkalis.

The *diacetyl* derivative melts at 125°; it is readily soluble in ether, chloroform, benzene, or hot alcohol:

0·2330 gave 15·4 c.c. moist nitrogen at 14° and 763 mm. N = 7·81.

$C_{20}H_{24}O_4N_2$ requires N = 7·86 per cent.

Chloraldiethylmalonamide, $CEt_2(CO{\cdot}NH_2)_2,CCl_3{\cdot}CHO$, is obtained by heating molecular proportions of the amide and chloral hydrate together with a few drops of concentrated hydrochloric acid on the water-bath for two hours. When crystallised from hot alcohol it forms colourless prisms which melt at 178°; it is fairly soluble in hot water or ether, readily so in acetone or hot alcohol:

0·2320 gave 19·0 c.c. moist nitrogen at 18° and 754 mm. N = 9·38.
0·2468 ,, 0·3480 AgCl. Cl = 34·97.

$C_9H_{15}O_3N_2Cl_3$ requires N = 9·15; Cl = 34·85 per cent.

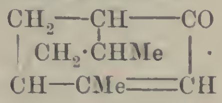
It is quite stable towards boiling water or hot dilute hydrochloric acid.

CHEMISTRY DEPARTMENT,
THE SIR JOHN CASS TECHNICAL INSTITUTE,
ALDGATE.

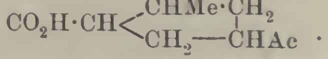
XXVIII.—*The Constitution of Umbellulone. Part II. The Reduction of Umbellulonic Acid.*

By FRANK TUTIN.

IN a previous communication on the constitution of umbellulone (Trans., 1906, **89**, 1104) it was shown that this ketone is most probably represented by the following formula:



It followed from this that umbellulonic acid, obtained by the oxidation of umbellulone with potassium permanganate, is represented by the formula:



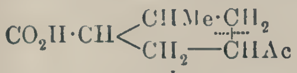
The correctness of these conclusions could not at that time be confirmed by direct experimental evidence, but this has now been accomplished.

Umbellulonic acid, $C_9H_{14}O_3$, has been submitted to the reducing action of sodium and alcohol, when a hydroxy-acid having the formula

$C_9H_{18}O_3$ was produced, and this readily gives a lactone (b. p. 246—248°; $[\alpha]_D - 13{\cdot}54°$) having the formula, $C_9H_{16}O_2$. It is evident, therefore, that the closed ring contained in umbellulonic acid had been opened during the reduction by the addition of two atoms of hydrogen. The hydroxy-acid obtained must therefore be a chain compound.

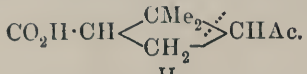
This hydroxy-acid, in the form of its potassium salt, is stable towards cold permanganate in neutral solution, and the keto-acid corresponding to it could not be obtained. When, however, it is treated with permanganate in presence of an excess of alkali, it undergoes oxidation with the formation of acetic and *iso*propylsuccinic acids.

In the previous communication (*loc. cit.*) it was shown that umbellulonic acid must contain either a methylpentamethylene or a dimethyltetramethylene ring. There are only two keto-acids containing either of these rings that are also capable of giving on reduction a hydroxy-acid, which, by subsequent oxidation, would yield acetic and *iso*propylsuccinic acids, namely, those possessing the following formulæ:



$$CO_2H\cdot CH\Big<\begin{matrix}CHMe\cdot CH_2\\ CH_2{-\!\!-}CHAc\end{matrix}$$

I.



$$CO_2H\cdot CH\Big<\begin{matrix}CMe_2\\ CH_2\end{matrix}\Big>CHAc.$$

II.

Each of these acids would give, by the opening of the ring on reduction at the place indicated by the dotted line, δ-hydroxy-α-*iso*propyl-*n*-hexoic acid, $CH_3\cdot CH(OH)\vdots CH_2\cdot CH_2\cdot CH(CO_2H)\cdot CHMe_2$, and this acid by undergoing oxidation at the position indicated, would yield acetic and *iso*propylsuccinic acids. The product of the reduction of umbellulonic acid must therefore be l-δ-*hydroxy*-α-iso*propyl*-n-*hexoic acid.*

Formula II represents the pinononic acid obtained by Wagner by the oxidation of pinene (*Ber.*, 1896, **29**, 881) and it was shown in the previous communication that umbellulonic acid is neither identical nor stereoisomeric with it. Umbellulonic acid must, therefore, be correctly represented by formula I, that is, by the formula previously assigned to it.

EXPERIMENTAL.

Formation of l-δ-*Hydroxy*-α-iso*propyl*-n-*hexoic Acid.*

Fifteen grams of umbellulonic acid were dissolved in 100 c.c. of absolute alcohol and the solution rendered alkaline by the addition of sodium ethoxide. Ten grams of sodium were then introduced in small pieces, and, when this had dissolved, a further 100 c.c. of alcohol, followed by 10 grams of sodium, were added. After the addition of water, the greater part of the alcohol was removed, and, on acidifying the alkaline aqueous liquid thus obtained, an oily acid separated. This was isolated by means of ether, and distilled under 120 mm. pressure, when it was evident that lactone formation ensued, as a considerable quantity of water was eliminated. The distillate was dissolved in ether, freed from any traces of acids by means of sodium carbonate, and the ethereal liquid washed, dried, and evaporated. On distilling the residual oil under the atmospheric pressure it was found to boil from 246—248°, and amounted to 11·3 grams:

0·1092 gave 0·2776 CO_2 and 0·0982 H_2O. C = 69·3; H = 10·0.
0·1163 „ 0·2951 „ „ 0·1049 H_2O. C = 69·2; H = 10·0.
0·0992 „ 0·2514 „ „ 0·0893 H_2O. C = 69·1; H = 10·0.
$C_9H_{16}O_2$ requires C = 69·2; H = 10·2 per cent.

This substance, as has been shown in the introductory portion of this paper, is the *lactone* of l-δ-*hydroxy*-α-iso*propyl*-n-*hexoic acid*; it is a colourless, mobile liquid, possessing a pleasant odour:

0·5229 dissolved in 25 c.c. of absolute alcohol gave $\alpha_D - 0°34'$ in a 2-dcm. tube, whence $[\alpha]_D - 13·54°$.

On boiling this lactone with a solution of potassium hydroxide, the *potassium* salt of the corresponding hydroxy-acid was readily formed. This has a lævorotation in aqueous solution, and when treated with dilute sulphuric acid gives *l*-δ-hydroxy-*α*-*iso*propyl-*n*-hexoic acid. This hydroxy-acid, in the cold, does not pass spontaneously into the corresponding lactone, but this change readily occurs under the influence of heat.

Silver l-δ-*hydroxy*-α-iso*propyl*-n-*hexoate* crystallises from hot water in colourless needles. On analysis:

0·1268 gave 0·0487 Ag. Ag = 38·4.
$C_9H_{17}O_3Ag$ requires Ag = 38·4 per cent.

Oxidation of l-δ-*Hydroxy*-α-iso*propyl*-n-*hexoic Acid with Potassium Permanganate. Formation of* iso*Propylsuccinic and Acetic Acids.*

About 10 grams of the lactone were dissolved in a considerable excess of hot aqueous potassium hydroxide, the solution cooled, and diluted to about 1·5 litres. A quantity of a 3 per cent. solution of potassium permanganate equivalent to between two and three atomic proportions of oxygen, was then added. Oxidation proceeded slowly, but after some hours the colour of the permanganate was discharged. The filtered liquid was concentrated to a small bulk, acidified with sulphuric acid, and distilled in steam, when a quantity (about 5 grams) of the original lactone slowly passed over. The distillate, which had an acid reaction, was rendered alkaline by the addition of sodium carbonate, and the lactone removed by means of ether, after which the alkaline liquid was acidified and again distilled in steam. The acids contained in the distillate were converted into their barium salts, and, from the latter, silver salts were prepared. These gave some silver *l*-δ-hydroxy-*a*-*iso*propyl-*n*-hexoate, but the mother liquors from this yielded a salt which, after recrystallisation from water, was analysed with the following result:

0·1803 gave 0·1158 Ag. Ag = 64·2.

$C_2H_3O_2Ag$ requires Ag = 64·6 per cent.

This salt was thus identified as silver acetate.

The liquid remaining in the distilling flask after the first steam distillation, and which contained the non-volatile products of the oxidation, was repeatedly extracted with ether, and the ethereal liquid washed, dried, and evaporated. By this means a syrupy residue was obtained which, on standing for some time, became crystalline. The solid acid thus obtained was recrystallised from benzene, after which it melted at about 117—118°. When heated to 180° it evolved gas and gave a strong odour resembling that of valeric acid, from which it appeared probable that it contained a little of a substituted malonic acid. It was therefore heated at 180° until evolution of gas ceased, after which, on standing for some time, it slowly solidified. It was then again crystallised from benzene, and was obtained in tufts of needles, which melted sharply at 120°.

0·1007 gave 0·1946 CO_2 and 0·0699 H_2O. C = 52·7; H = 7·7.

$C_7H_{12}O_4$ requires C = 52·5; H = 7·5 per cent.

0·1619 required 20·3 c.c. of *N*/10 NaOH for neutralisation.

$C_5H_{10}(CO_2H)_2$ requires 20·2 c.c.

This acid had the same melting point (120°) as a specimen of *iso*propylsuccinic acid obtained from Prof. Crossley, and was evidently identical with it, as a mixture of the two preparations also melted at the same temperature. For the purpose of confirming the identity of the solid acid (obtained by the oxidation of *l*-δ-hydroxy-*a*-*iso*propyl-*n*-hexoic acid) with *iso*propylsuccinic acid, the remaining quantity of the former was converted into the ammonium salt, and this heated at 160° for four hours. In this way an imide was obtained which crystallised from water in plates melting at 62°, and a mixture of this substance with *iso*propylsuccinimide also melted at this temperature.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

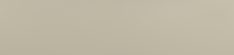
XXIX.—*The Reduction of Hydroxylaminodihydroumbelluloneoxime.*

By Frank Tutin.

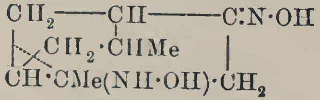
It was shown by Power and Lees (Trans., 1904, **85**, 636) that when umbellulone is treated with an excess of hydroxylamine in alcoholic solution, hydroxylaminodihydroumbelluloneoxime is formed. The present author has submitted this compound to the reducing action of sodium and alcohol with the object of ascertaining the properties of the resulting basic product, and whether it consisted of a single substance or a mixture of optical isomerides, such as had been observed to be formed by the reduction of *l*-methoneoxime (Tutin and Kipping, Trans., 1904, **85**, 65).

It has been shown (Lees, Trans., 1904, **85**, 644) that when bromodihydroumbellulone is reduced with sodium and alcohol, and that when umbellulone itself is submitted to this treatment (Tutin, Trans., 1906, **89**, 1118), one of the closed rings contained in the umbellulone molecule is opened by the addition of two atoms of hydrogen. In the preceding paper (" The Constitution of Umbellulone. Part II.") it is shown that a similar opening of the ring occurs when umbellulonic acid is reduced by the same reagent. It would therefore appear that the capability of addition of two atoms of hydrogen on treatment with sodium and alcohol is a property of that ring contained in the umbellulone molecule which is also present in umbellulonic acid. Taking this into consideration, it would appear probable that hydroxylaminodihydroumbelluloneoxime would on reduction give aminotetrahydroumbellulylamine, and not aminodihydroumbellulylamine, as might have been expected. The difference in the percentage composition of the respective salts and derivatives of these two bases is very small, and, from the results afforded by the analysis of the dihydrochloride, dibenzoate, and dibenzoyl derivative of the base obtained, it is impossible to say with certainty whether the latter has the formula $C_{10}H_{20}N_2$ or $C_{10}H_{22}N_2$. Considering all the facts, however, it is most probable that it is aminotetrahydroumbellulylamine, $C_{10}H_{22}N_2$.

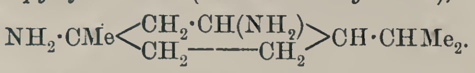
It has been shown (Trans., 1906, **89**, 1105, and preceding paper) that umbellulone possesses a constitution represented by the following formula :


.

Hydroxylaminodihydroumbelluloneoxime, being analogous in its properties to hydroxylaminodihydrocarvoneoxime (*Ber.*, 1898, 31, 1810), will therefore be represented by the following formula:



If, as appears probable, the opening of the ring on the reduction of this compound takes place at the same point as in umbellulonic acid when reduced (*loc. cit.*), namely, at the point indicated by the dotted line, then aminotetrahydroumbellulylamine will be 1 : 3-*diamino*-1-*methyl*-4-iso*propyl*cyclo*hexane* (1-*aminomenthylamine*),



$$NH_2\cdot CMe{<}\begin{matrix}CH_2\cdot CH(NH_2)\\ CH_2\text{———}CH_2\end{matrix}{>}CH\cdot CHMe_2.$$

Aminotetrahydroumbellulylamine is a liquid (b. p. 136—138°/50 mm.) possessing a not very marked basic odour. It dissolves in water with the development of heat, and has a specific rotatory power, calculated from that of its dihydrochloride, of $-18{\cdot}8°$. The *sulphate* and Reychler's d-*camphorsulphonate* were prepared from it, but were found to be uncrystallisable, deliquescent syrups. *Aminotetrahydroumbellulylamine dibenzoate* crystallises in needles which melt at 212—213°; the *dihydrochloride* also forms needles, but it is infusible at 305°. *Dibenzoylaminotetrahydroumbellulylamine* crystallises in prisms or in leaflets, which melt at 194°.

EXPERIMENTAL.

The hydroxylaminodihydroumbelluloneoxime used in this investigation was prepared as follows. A concentrated aqueous solution of hydroxylamine hydrochloride (62 grams) was mixed with a solution of sodium ethoxide (prepared by dissolving 20 grams of sodium in 300 c.c. of alcohol), and 34 grams of umbellulone were added. The mixture was boiled for two hours, and the greater part of the alcohol removed by distillation. After dilution with water the mixture was acidified with sulphuric acid. The undissolved oil was subsequently removed by extraction with ether, after which the acid aqueous liquid was rendered alkaline by the addition of sodium carbonate, and the hydroxylamino-oxime isolated by means of ether. The yield was 35 grams.

Aminotetrahydroumbellulylamine, $C_{10}H_{22}N_2$.—The hydroxylaminodihydroumbelluloneoxime, prepared as described above, was dissolved in 600 c.c. of absolute alcohol, and 60 grams of sodium introduced in small pieces. The mixture was not cooled, but allowed to boil vigorously. After all the sodium had dissolved, the whole was distilled with steam as long as the condensed liquid had an alkaline reaction. The distillate, which contained some oil, was collected in hydrochloric acid, but the oil did not dissolve. When the distillation was complete, the entire acidified distillate was evaporated to a small bulk and freed from a small amount of non-basic oil by means of ether. The concentrated acid liquid was then made strongly alkaline by the addition of potassium hydroxide, when an oily liquid separated. This was extracted with ether, the ethereal liquid washed with a little water, and dried with anhydrous potassium carbonate. On removing the ether, the base was obtained as a colourless liquid, which, on distillation under 50 mm. pressure, boiled between 136° and 138°. The substance was not quite pure, but contained a very small quantity of another base. The whole of the distillate was, therefore, dissolved in a slight excess of dilute sulphuric acid, when a crystalline sulphate separated which was practically insoluble in cold water. This was collected, but amounted only to 0·2 gram; it melted at 199°. The filtrate, which contained the *aminotetrahydroumbellulylamine sulphate*, was concentrated in a vacuum, but did not crystallise, and the base was therefore again liberated.

Aminotetrahydroumbellulylamine is a liquid which readily absorbs carbon dioxide from the atmosphere. When mixed with about an equal quantity of water, considerable heat is developed and a homogeneous liquid is obtained, but on the addition of a little more water an oil separates, which, however, is redissolved on further dilution.

Aminotetrahydroumbellulylamine Dihydrochloride, $C_{10}H_{22}N_2,2HCl$.—A portion of the base was dissolved in water, and dilute hydrochloric acid added until the liquid had an acid reaction. As it was found that dissociation occurred when this solution was heated, it was concentrated in a vacuum over sulphuric acid, when it eventually formed a hard, partly crystalline mass. This was dissolved in boiling alcohol and the solution concentrated, after which the dihydrochloride separated in colourless prisms, which, when heated to 305°, did not melt but slowly decomposed:

0·1071 gave 0·1940 CO_2 and 0·0924 H_2O. C = 49·4; H = 9·6.
0·2489 ,, 25·0 c.c. of nitrogen at 22° and 760 mm. N = 11·4.
0·1389 ,, 0·1637 AgCl. Cl = 29·1.
0·1051 ,, 0·1188 AgCl. Cl = 29·0.
$C_{10}H_{20}N_2,2HCl$ requires C = 49·8; H = 9·1; N = 11·6; Cl = 29·4 per cent.
$C_{10}H_{22}N_2,2HCl$,, C = 49·4; H = 9·9; N = 11·5; Cl = 29·2 ,, ,,

The optical rotation of the dihydrochloride was determined in absolute alcohol and in water:

0·4086 dissolved in 25 c.c. of absolute alcohol gave $\alpha_D - 0° \ 42'$ in a 2-dcm. tube, whence $[\alpha]_D - 21·41°$.

0·4086 dissolved in 25 c.c. of water gave $\alpha_D - 0° 26'$ in a 2-dcm. tube, whence $[\alpha]_D - 13·25°$. The specific rotatory power of the base, calculated from that of the dihydrochloride is $[\alpha]_D - 18·8°$.

Aminotetrahydroumbellulylamine dihydrochloride dissolves in water with great readiness; it is moderately soluble in alcohol, and almost insoluble in ethyl acetate. In a mixture of ethyl acetate and alcohol it dissolves more readily in the cold than when heated.

Aminotetrahydroumbellulylamine Dibenzoate, $C_{10}H_{22}N_2.2C_7H_6O_2$.—To an aqueous solution of the base, a slight excess of benzoic acid was added, and on evaporation in a vacuum over sulphuric acid a hard crystalline mass was obtained. This was dissolved in boiling alcohol, and the liquid concentrated, after which the salt separated in colourless prisms which melted at 212—213°, and this melting point was not altered by further crystallisation:

0·1042 gave 0·2660 CO_2 and 0·0755 H_2O. C = 69·6; H = 8·1.
$C_{10}H_{20}N_2,2C_7H_6O_2$ requires C = 69·9; H = 7·7 per cent.
$C_{10}H_{22}N_2,2C_7H_6O_2$,, C = 69·5; H = 8·2 ,, ,,

The optical rotation of the dibenzoate was determined in water and in absolute alcohol. 0 4244, dissolved in 25 c.c. of absolute alcohol, gave $\alpha_D - 0° 18'$ in a 2-dcm. tube, whence $[\alpha]_D - 8·83°$. 0·4244, dissolved in 25 c.c. of water, gave $\alpha_D - 0° 15'$ in a 2-dcm. tube, whence $[\alpha]_D - 7·36°$. The specific rotation of the base, calculated from that of its dibenzoate, is $[\alpha]_D - 17·9°$.

A quantity of the dibenzoate was fractionally crystallised from alcohol, but all the crops of crystals obtained were indentical and had a uniform melting point of 212—213°.

Dibenzoylaminotetrahydroumbellulylamine, $C_{10}H_{20}N_2(CO·C_6H_5)_2$.—The base obtained from either the pure dibenzoate or the pure dihydrochloride, when benzoylated by means of the Schotten-Baumann method, gave a product which, when crystallised from alcohol, melted at 194°. On fractional crystallisation this was found to be homogeneous.

0·0990 gave 0·2762 CO_2 and 0·0691 H_2O. C = 76·1; H = 7·8.
0·2642 ,, 16·6 c.c. of nitrogen at 20° and 776 mm. N = 7·3.
$C_{10}H_{18}N_2(CO·C_6H_5)_2$ requires C = 76·6; H = 7·4; N = 7·4 per cent.
$C_{10}H_{20}N_2(CO·C_6H_5)_2$,, C = 76·2; H = 7·9; N = 7·4 ,, ,,

The optical rotation of the dibenzoyl derivative was determined in chloroform solution. 0·5379, dissolved in 25 c.c. of chloroform, gave $\alpha_D + 5° 3'$ in a 2-dcm. tube, whence $[\alpha]_D + 117·3°$.

Dibenzoylaminotetrahydroumbellulylamine is readily soluble in chloroform and nearly insoluble in water. When crystallised from absolute alcohol, in which it is moderately soluble, it separates in short stout prisms, but from dilute alcohol it is obtained in long leaflets; occasionally both forms of crystals are simultaneously deposited.

As the most readily soluble portions obtained by the fractional crystallisation of the dibenzoate and the dihydrochloride did not crystallise with facility, the base which they contained was benzoylated and the resulting dibenzoyl derivative submitted to a systematic process of fractional crystallisation. The only substance which could be obtained in a state of purity from this was the dibenzoyl derivative melting at 194°, and this represented by far the greater part of the material. Nevertheless, the two most readily soluble fractions were oily in character, and were evidently mixtures, as they could only with difficulty be induced to crystallise. The substances contained in these mixtures, other than the benzoyl derivative described, were probably benzoyl derivatives of bases stereoisomeric with aminotetrahydroumbellulylamine, but they were present in so small an amount that their isolation was impossible without employing a very much larger quantity of material than was available.

The Wellcome Chemical Research Laboratories,
London, E.C.

XXX.—*Some Constituents of Natural Indigo. Part I.*

By Arthur George Perkin and W. Popplewell Bloxam.

It is well known that natural indigo contains, in addition to indigotin and indirubin, certain impurities such as indigo-brown, indigo-gluten, mineral matter, and frequently traces of kaempferol. Indigo-brown and indigo-gluten have been but little examined, for not only do they possess a somewhat uninviting nature, but their general reactions do not indicate any points of special interest. The present work has originated from a desire to improve the present methods of indigo analysis, and this it appeared could only be accomplished by the isolation and subsequent examination of the properties of these impurities. As a result, a new analytical method has been devised, termed the "tetrasulphonate" process, and a description of this has already been given by one of us (*J. Soc. Chem. Ind.*, 1906, 25, 735). In connexion with indigo-brown, the subject of this paper, it was important to determine if any relationship existed between this substance and indigotin itself, for should such be the case, an explanation could thus be suggested as to the somewhat unsatisfactory yields of indigo which are obtained from the plant.

Literature on the subject of indigo-brown is extremely meagre, and appears to be confined to the communications of Chevreul (Gmelin, *Handbook of Chem.*, 1859, **13**, 48) and Berzelius (*ibid.*). In order to isolate this product, the latter chemist digested powdered indigo with boiling dilute sulphuric acid to remove the gluten, and subsequently with potassium hydroxide solution to dissolve the brown. The alkaline liquid was neutralised with acetic acid, evaporated to dryness, the residue digested with boiling alcohol, and the solution evaporated. Thus obtained, the indigo-brown consisted of a dark coloured, transparent resin, sparingly soluble in alcohol, but readily so in alkaline solutions. It contained nitrogen, and on dry distillation evolved ammonia together with some quantity of an empyreumatic oil.

Schunck, during his well-known researches on indican, prepared from this substance by means of dilute acids (*Phil. Mag.*, 1855, [iv], **10**, 74, and *ibid.*, 1858, **15**, 127) various brown, amorphous products, for example, α-indifulvin, $C_{22}H_{20}O_3N_2$; β-indifulvin, $C_{44}H_{38}O_8N_4$; indifuscin, $C_{24}H_{20}O_3N_2$; indifuscone, $C_{22}H_{20}O_8N_2$; indiretin ($C = 66·04$; $H = 5·57$; $N = 3·83$); and indihumin, $C_{10}H_9O_3N$.

The latter compound Schunck considered was, perhaps, identical with indigo-brown, and described it as a brown powder insoluble in water and alcohol, but soluble in alkalis. With nitric acid it gave an orange-yellow, amorphous product.

Somewhat later, Schunck and Roemer (*Ber.*, 1879, **12**, 2311) studied the action of hydrochloric acid on indican in the absence of air. Indigotin was not formed, but a brownish-yellow precipitate quickly separated, which was partly soluble in alkali. Experiments carried out with the object of converting this product into indigotin were unsuccessful.

EXPERIMENTAL.

Finely powdered crude Bengal indigo containing approximately 62 per cent. of indigotin was digested with boiling dilute hydrochloric acid to remove the gluten, during which operation it lost 21·5 per cent. in weight. Experiment showed that pyridine, probably the only suitable solvent for this purpose, readily extracted indigo-brown from the residue, and that for this object merely a short digestion at the boiling point was necessary. After cooling, the mixture was filtered and the residue washed with cold pyridine as long as the filtrate possessed a brownish-red colour, the final washings, which contained a trace of indigotin, being neglected. In this manner the indigo suffered a further loss of 18·03 per cent., and was then found to contain 91·1 per cent. of indigotin.

The pyridine filtrate was evaporated to a small bulk, and while hot was treated with twice its volume of alcohol, causing the separation of a brown precipitate, which was collected and repeatedly washed with boiling alcohol. As the final washings possessed a reddish tint, an indication of the presence of indirubin, the product was again dissolved in pyridine and reprecipitated with alcohol, but as this did not appear to effect a complete separation of the impurity it was extracted with boiling acetic acid until an almost colourless filtrate was produced. An analysis of the substance now revealed the presence of about 4 per cent. of mineral matter, and this could only be successfully removed by adding its solution in pyridine to hot dilute hydrochloric acid. The precipitate was collected, washed with dilute acid, then with water, and, finally, again extracted with acetic acid and dried at 100°. Before analysis it was heated to 160°, and in this manner frequently lost 10 per cent. by weight.

Found, $C = 68{\cdot}47$, $68{\cdot}53$, $68{\cdot}34$, $68{\cdot}46$; $H = 4{\cdot}18$, $4{\cdot}13$, $4{\cdot}30$,— ; $N = 9{\cdot}95$, $9{\cdot}84$.

$C_{16}H_{12}O_3N_2$ requires $C = 68{\cdot}57$. $H = 4{\cdot}28$; $N = 10{\cdot}0$ per cent.

In carrying out the nitrogen estimations of this and the other brown compounds referred to in this paper, it was found that the gas was evolved much more slowly than is usually the case, fully one hour longer being required for the operation.

This substance, which forms the main constituent of the pyridine extract, closely resembles in general properties the indigo-brown of Berzelius and the indihumin of Schunck (*loc. cit.*), and consists of a brown powder insoluble in alcohol, but soluble in alkaline solutions with a deep brown coloration. The figures required by Schunck's formula, $C_{10}H_9O_3N$ ($C = 62{\cdot}63$; $H = 4{\cdot}71$; $N = 7{\cdot}33$), are not in agreement with those given above, and it thus appears that the two compounds cannot be identical. On the other hand, the fact that it is only completely dehydrated at 160° and the nitrogen difficulty referred to above may possibly account to some extent for this disparity. It is practically insoluble in all the usual solvents with the exception of hot pyridine, and its properties are of an uninteresting nature. On dry distillation, it gives off yellowish-brown vapours having an alkaline reaction, and which condense to form a small quantity of oily matter of the same colour, as noted by Berzelius, and its behaviour with nitric acid is in accordance with the statement of Schunck. It is readily reduced by zinc dust in alkaline solution with formation of a pale brown liquid, which, on neutralisation with acid, deposits a precipitate of the same colour, and this does not appear to reoxidise on standing in air. By means of acetic anhydride and sulphuric acid it is probably converted into an acetyl compound, which differs but little in property from the original substance, except that it is less readily attacked by alkaline solutions. With acetic anhydride and zinc dust the acetyl derivative of its reduction product is certainly formed, and this consists of a pale brown, amorphous powder somewhat readily soluble in alcohol.

Action of Boiling Potassium Hydroxide Solution.—4·5 grams of the substance $C_{16}H_{12}O_3N_2$ were digested with 50 c.c. of a 50 per cent. potassium hydroxide solution for one hour at the boiling point in an open flask. The product dissolved with considerable difficulty, and as the liquid became more concentrated, a tarry precipitate, evidently consisting of a potassium salt, commenced to separate. The mixture, diluted with water, was carefully neutralised with sulphuric acid, and the resulting brown precipitate collected and washed. It weighed 2·85 grams.

The filtrate and washings were evaporated to dryness, the mass extracted with boiling alcohol, and the extract itself then evaporated. The crystalline residue was treated with water, the solution filtered from a trace of flocculent matter, neutralised with alkali and rendered faintly acid with acetic acid. Ether removed from this liquid a colourless acid, which was purified by crystallisation from benzene.

Found, N = 10·22. $C_7H_7O_2N$ requires N = 10·21 per cent.

It formed colourless prisms melting at 143—144°, and evidently consisted of anthranilic acid.

The brown residue, 2·85 grams, was again submitted to the action of the boiling alkali, by which means it was further reduced to 2·2 grams, a small quantity of anthranilic acid being thus produced. In a third treatment it was practically unattacked. These results are interesting and indicate that the substance $C_{16}H_{12}O_3N_2$ consists probably of a complex indoxyl derivative, which may be either derived from indoxyl alone or result from its condensation with some second substance derived from the indigo plant. With the hope of obtaining some further information on this point, it seemed desirable to determine the composition of the brown residue which was not attacked by the alkali.

For purification the product was dissolved in pyridine, filtered from a trace of insoluble matter, and the filtrate poured into dilute hydrochloric acid and thoroughly washed. For analysis it was dried at 160°.

Found, C = 71·39, 71·29; H = 4·05, 4·23; N = 7·94, 7·92 per cent.

It would not be of value to speculate as to the formula of this product, for which no simple expression appears to be available. It is interesting to note, however, that it contains a considerable quantity of nitrogen. It possesses a more olive tint than the substance $C_{16}H_{12}O_3N_2$, but its properties are of a similar nature. These call for no special note, and are of an uninteresting character.

Indirubin.

The alcoholic pyridine filtrates from the substance $C_{16}H_{12}O_3N_2$, on partial evaporation and standing, deposited crystals which were collected on the pump, washed with a mixture of pyridine and alcohol, and finally crystallised from nitrobenzene, employing animal charcoal.

Found, $C = 72{\cdot}94$; $H = 4{\cdot}09$; $N = 10{\cdot}72$.

$C_{16}H_{10}O_2N_2$ requires $C = 73{\cdot}28$; $H = 3{\cdot}82$; $N = 10{\cdot}69$ per cent.

It formed long, glistening needles soluble in boiling acetic acid with a violet-red colour, and had all the reactions assigned to indirubin. The identity of natural and artificial indirubins, about which there was formerly some controversy, is now fully established (Marchlewski and Radcliffe, *J. Soc. Chem. Ind*, 1898, **17**, 434), and no difference could be observed between the above-mentioned sample and one that had been synthetically prepared.

The amount present in the Bengal indigos examined was very small, and in one case only 5 grams were obtained from 5 lb. of the dye-stuff. As a result of experiments, no Bengal indigo has been found which, when analysed by the above method, did not contain traces of indirubin.

In Java indigos, as is well known, large quantities of this substance, are frequently present, and this is due to certain special processes which are employed during the manufacture of the colouring matter from the plant.

The more soluble Constituents of Indigo-Brown.

The mother liquor from which the indirubin had been removed on further treatment with alcohol deposited a small quantity of a brown, amorphous precipitate, which was collected, repeatedly washed with boiling alcohol and dried. It was now digested with boiling acetic acid, filtered from insoluble matter, evidently consisting of the above-described substance $C_{16}H_{12}O_3N_2$, the liquid allowed to stand overnight, and filtered again if necessary. The acetic acid solution was treated with boiling alcohol, causing the separation of a brown precipitate, which was removed and well washed with alcohol. Examination showed that it was contaminated with mineral matter, and it was therefore dissolved in pyridine, the solution poured into dilute hydrochloric acid, and the product collected. Analysis of the substance, dried at 160°, gave:

Found, $C = 66{\cdot}13$; $H = 4{\cdot}84$; $N = 9{\cdot}85$.

$C_{24}H_{22}O_5N_3$ requires $C = 66{\cdot}66$; $H = 5{\cdot}09$; $N = 9{\cdot}72$ per cent.

It consisted of a brown powder identical in appearance with the substance $C_{16}H_{12}O_3N_2$, but differed from this compound in that it was soluble in acetic acid. In general properties, however, the two products are so similar that no detailed account is necessary in this case. The amount of this substance present in indigo-brown is so small that extended experiment was not possible, but sufficient was available to determine that on long digestion with boiling potassium hydrate solution, anthranilic acid is formed, and that the reaction appears to follow a similar course to that which was observed with the substance $C_{16}H_{12}O_3N_2$.

The alcoholic pyridine filtrate from the compound $C_{24}H_{22}O_5N_3$ deposited some crystals of indirubin, which were removed, and the filtrate was treated with alcohol. The precipitate thus formed was neglected, and the clear liquid diluted with its own volume of benzene and evaporated to a small bulk. On cooling, a brown, amorphous powder separated which was collected and washed with benzene. Examination showed that this product was contaminated with a red colouring matter, and to remove this it was dissolved in alcohol, the solution poured into ether, and the ethereal liquid extracted with dilute alkali. The brown-coloured extract was neutralised with hydrochloric acid, the precipitate collected, and very thoroughly washed. For analysis it was dried at 160°:

Found, $C = 64{\cdot}86$; $H = 4{\cdot}81$; $N = 9{\cdot}27$.

$C_{16}H_{14}O_4N_2$ requires $C = 62{\cdot}43$; $H = 4{\cdot}69$; $N = 9{\cdot}39$ per cent.

This compound, which is present in indigo-brown in but trifling amount, consists of a pale brown, amorphous powder, and is distinguished from the above-described brown substances by its ready solubility in alcohol, and the fact that when heated it gives a voluminous charcoal. Its general properties are, however, so similar to the other brown products as not to merit description.

The alcoholic benzene filtrate from which the above described compound had been isolated was evaporated to dryness, the residue dissolved in ether containing a trace of alcohol, and the solution extracted with dilute alkali in order to remove a small quantity of brown substance which was still present. The ethereal solution, on evaporation, yielded a crystalline residue which was washed two or three times with boiling light petroleum and purified by recrystallisation from nitrobenzene. This substance was indirubin, which is evidently, therefore, the only red compound present in the Bengal indigos examined during the progress of this work. The statement by one of us (W. P. Bloxam, Trans., 1905, **87**, 979) that indigo contains a non-nitrogenous red substance cannot thus be accurate, and arose from the contamination of the product with secondary compounds, which interfered with the satisfactory operation of the well-known qualitative method for the detection of nitrogen when applied to it.

Again, the statement of Bergtheil (*Report of the Indigo Research Station, Sirsiah*, 1906), "Preliminary examination . . . has shown decisively that there is more than one red body in most commercial indigos," is difficult to understand, at least as regards the Bengal variety, and his further results will be awaited with interest.

The light petroleum extracts from the crude indirubin isolated in the above-described manner were decolorised with animal charcoal and evaporated. An oily residue was thus obtained which became semi-solid on standing, and had the properties of a wax. The amount isolated was minute in respect of the quantity of indigo extracted. By exhausting the dried leaves of the *Indigofera arrecta* and *I. Sumatrana* with boiling alcohol, wax-like compounds were obtained of a very similar nature, which, however, did not appear to merit careful examination.

The investigation of a sample of Java indigo showed that this contained a brown product probably identical with that isolated from the Bengal variety, but in smaller amount. Some quantity of crystalline indirubin was also prepared from it.

Action of Boiling Dilute Acids on the Leaf Extract.

An aqueous extract of the air-dried leaf of *I. Sumatrana* (1000 grams) was evaporated to dryness, incorporated with sand, and extracted with alcohol. After removal of the alcohol, the residue was dissolved in water and digested at the boiling point with 10 c.c. of hydrochloric acid for one hour, and the mixture then allowed to stand overnight. 3·5 grams of a dark-coloured, resinous product had separated, which was collected and treated with alcohol, by which means a small quantity of crystalline indigotin (0·05 gram) remained undissolved. As an examination of the aqueous filtrate indicated the absence of indoxyl or other substances convertible into indigo by oxidation, this result is fully in harmony with the experiments of Schunck and Roemer (*loc. cit.*) on the action of hydrochloric acid on indican in the absence of air.

The alcoholic extract of the resinous substance on treatment with ether gave a reddish-brown precipitate, which was collected and well washed. For purification it was treated with cold alcohol, the residue dissolved in pyridine, and poured into dilute hydrochloric acid with the object of removing a trace of mineral matter which adhered to it somewhat tenaciously. After being dried at 160°, it was found to contain N = 5·67, and a second preparation gave C = 66·04; H = 5·00 per cent.

This product, though somewhat redder in appearance, had many properties in common with the indigo-brown substances described in this paper, but the low percentage of nitrogen it contains shows that it is more closely allied to the brown compounds that Schunck (*loc. cit.*) prepared from his indican.

On the other hand, as but a crude plant extract had been employed, it was quite possible that the brown compounds produced in this manner would be contaminated with non-nitrogenous impurities. The latter might, for instance, consist of the well-known reddish-brown anhydrides or phlobophanes which are obtained when solutions of catechol-tannins are boiled with dilute acids, and this was quite possible, as the work of Bergtheil (Trans., 1904, **85**, 876) has indicated the presence of tannin in the leaf. To confirm this point, application was made to Prof. H. R. Procter, who was kind enough to allow analyses of the air-dried leaves of *Indigofera arrecta* and *Sumatrana* to be carried out in his laboratory, with the following result:

	Indigofera arrecta.	*Indigofera Sumatrana.*
Tannin matter absorbed by hide	2·6	1·6
Soluble non-tannin matters	30·4	38·4
Insoluble in water at 15°	55·5	52·1
Water	11·5	7·9

During these analyses a considerable amount of the indican present in the leaf was hydrolysed, presumably by its own ferment, and the separated indigotin was deposited amongst the hide-powder. Again, it is well known that hide-powder is apt, to some extent, to carry down substances other than tannins, so that it is evident that these varieties of *Indigofera* contain little if any tannin matter. On the other hand, if a compound capable of producing, as is anticipated, non-nitrogenous brown substances exists in the leaf, the presence of only a minute quantity is necessary to explain the point under discussion. During the "isatin" process which has been employed by Orchardson, Wood, and Bloxam (*loc. cit.*) for the analysis of the leaves, it was noted that in addition to indirubin certain brown products soluble in alkali are simultaneously formed, but it has not yet been possible to determine if these contain nitrogen.

When the compound $C_{16}H_{12}O_3N_2$ is dissolved in an alkaline hydrosulphite solution, and the liquid allowed to stand at 50—60° even for several days, no indigotin separates on oxidation, so that the frequently asserted superiority of the natural over the artificial variety of indigo, if correct, cannot be accounted for in this manner.

Summary.

The results of this investigation tend to strengthen the suspicion that the constituents of indigo-brown are derived from indoxyl during the manufacture of indigo from the plant. The fact that they are partially converted into anthranilic acid on boiling with strong alkali, and that their carbon percentage composition can be approximately represented as a multiple of C_8, together with their high percentage of nitrogen, harmonises with this view. On the other hand, it suggests itself as possible that although they are derivatives of indoxyl, these compounds need not necessarily be produced during the manufacture, and may be formed from some substance other than indican present in the plant. That on boiling the leaf extract with dilute acid a somewhat similar brown product is formed, tends at first sight to confirm this view, but the question had then to be answered as to what becomes of the indoxyl during this operation, for little or no indigotin, owing to the absence of oxidising agents, is or can be produced. Schunck and Roemer (*loc. cit.*), who studied this reaction with indican in the cold, as previously stated, obtained an amorphous condensation product from this substance, though it is to be noted that some doubt now exists as to the purity of their compound in view of the isolation of crystalline indican by Hoogewerff and ter Meulen (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 520). That indoxyl, however, does condense in this manner seems certain, for Hazewinkel (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 152) states that when indoxyl is boiled with acid it changes into a red substance and emits a pungent odour. Rawson, again (*Report on the Cultivation and Manufacture of Indigo*, Mozufferpore, 1904, p. 86), says: "The blower . . . . by quickly getting rid of CO_2 gas . . . . prevents decomposition of a portion of the colouring matter into worthless brown substances, which takes place to a greater extent under other conditions." We have also noted that aqueous extracts of indigo leaf, on long standing, gradually exhibit a decrease in the quantity of indigotin produced by analysis, and this appears to be due to a secondary condensation of the character under discussion. Beyerinck (*Proc. Roy. Acad. Scien. Amsterdam*, 1899, 120), in a paper "on the formation of indigo from woad (*Isatis tinctoria*)," finds that the action of excess of air on a dying woad leaf causes a loss of indoxyl with formation of unknown colourless and brown substances. Again, he states that "strong acids, just as alkalis, though in a far less degree, favour the formation of indigo from indoxyl, but then part of this substance constantly changes into a brownish-black matter." Finally, "during the slow dying of the leaves of *Indigofera* plants in CO_2 containing air, a small quantity of a brown pigment is formed," and ". . . . many other indigo plants give in place of indigo a black or a brown pigment."

As regards the yield of indigo from the plant, Bergtheil (*loc. cit.*) considers that at least 87 per cent. of the theoretical yield of indigotin is accounted for in the manufacturing operation, including 5 per cent. remaining in the leaves after the steeping process, and 10 to 20 per cent. which is lost in the decantation of the supernatant liquid, or "seet" water. On the other hand, a difference of opinion exists as to the actual amount of indigotin which any given sample of the plant is capable of yielding. Very recently Rawson's ingenious persulphate process (*loc. cit.*) for the determination of indigotin from the leaf has been modified by Bergtheil (*J. Soc. Chem. Ind.*, 1906, **25**, 735), and independently by Orchardson, Wood, and Bloxam (*ibid.*, 1907, **26**, 4), with the result that higher values are now given by it. The latter three authors, however, employing the isatin process suggested to them by Prof. Beyerinck of Delft, by which means the indoxyl is estimated as indirubin, have obtained considerably enhanced figures over those given by the persulphate method, and these results, though given with some reserve, are exceedingly suggestive. In any case some loss remains to be accounted for, and this, we suggest, is probably to be found in the formation of indigo-brown.

The final answer to this and other questions connected with the manufacture of natural indigo can only be given with certainty by a study of the pure glucoside indican, and this we hope shortly to be in a position to communicate to the Society. The isolation of this substance from the leaf in the crystalline condition is by no means an easy matter, and at best a long and tedious process, and Hoogewerff and ter Meulen (*loc. cit.*), its discoverers, obtained but 5 grams from 17 kilos. of the raw material. Though we have been successful in preparing the pure compound from the leaves of *Indigofera arrecta*, the yield was also poor, and we are at present studying a method which we believe will result in the production of a much larger quantity of this exceedingly rare compound.

Our thanks are due to Messrs. I. Q. Orchardson and S. H. Wood, who very kindly undertook the preparation of the crude indigo-brown for this investigation.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS.

XXXI.—*The Alkylation of* d-*Fructose.*

By THOMAS PURDIE, F.R.S., and DAVID MCLAREN PAUL, B.Sc.,
Carnegie Scholar.

PREVIOUS communications from this laboratory (Trans., 1903, **83**, 1021 and subsequent papers) have shown that the hydroxyl groups of methylaldosides can be completely methylated by methyl iodide and dry silver oxide, and that the methylated aldosides so obtained yield on hydrolysis methyl ethers of the respective aldoses. The latter compounds can be reconverted into methylated aldosides by condensation with methyl alcohol containing hydrogen chloride, or by the silver oxide method of alkylation; in general a mixture of stereoisomeric aldosides is thus produced, the former process giving the α-aldoside, the latter the β isomeride in larger proportion. The object of the present research was to ascertain if ketoses behave similarly to aldoses in the above series of reactions. The methylfructoside required for our experiments was prepared from pure *d*-fructose by Fischer's method (*Ber.*, 1895, **28**, 1160). Fischer himself failed to obtain the substance in the crystalline state, and our efforts towards this end were also unsuccessful. We therefore used, as starting material, the syrup left after removal of hydrogen chloride and evaporation of the methyl alcohol. This crude material is doubtless, in the main, a mixture of α- and β-methylfructosides, although so far no evidence has been adduced with respect to the existence of stereoisomeric alkylketosides. As appears in the sequel, it probably contains also an isomeric, less lævorotatory, or possibly dextrorotatory hexoside and, according to Fischer, a considerable proportion of unaltered fructose.

We find that the alkylation of this syrupy mixture by means of methyl iodide and silver oxide, and the hydrolysis of the resulting mixture of tetramethyl methylketosides, proceed, in general, in the same manner as in previous similar experiments with aldosides. Greater difficulty was, however, experienced in isolating the products, and the rotatory powers observed in different preparations varied considerably. We attribute these anomalies to the mixed nature of the initial fructoside material, and to the greater susceptibility of ketoses and their derivatives to oxidation and other chemical changes. By-products are thus introduced which fractional distillation fails to remove completely.

The tetramethyl methylfructoside obtained by alkylation of methylfructoside, and the product of its hydrolysis, tetramethyl fructose, proved to be uncrystallisable syrups, which could, however, be distilled without decomposition, and were thus isolated. The syrupy tetramethyl fructose was reconverted into tetramethyl methylfructoside by the silver oxide process; the liquid fructoside so obtained gave on hydrolysis again a syrupy tetramethyl fructose, from which, however, the pure methylated sugar eventually separated in well-formed crystals. This in turn was converted into the fructoside by Fischer's method and also by the silver oxide process. Both products being uncrystallisable liquids, the α- and β-forms could not be separated, but, on the evidence of its lower lævorotation, the fructoside from the latter process contained the β-form in greater proportion. Crystalline tetramethyl fructose was recovered from both products on hydrolysis.

Methylfructoside.

This compound and the parent hexose should, presumably, exist in two stereoisomeric forms corresponding to the α- and β-alkylaldosides and aldoses. In order to detect the production of the two methylfructosides during the condensation of fructose with methyl alcohol, this process, and the subsequent hydrolysis of the fructoside, were followed by polarimetric observations. Ordinary fructose shows in aqueous solutions a downward mutarotation in the lævo sense $[\alpha]_D - 104° \longrightarrow - 92°$. Assuming on the analogy of glucose that the stable crystallised sugar is the α-form ($[\alpha]_D$ − 104°), the specific rotation of the β-fructose should be numerically less than − 92°, and the α- and β-fructosides respectively more and less lævorotatory than the corresponding forms of the sugar. β-Methylfructoside, like the β-alkylaldosides, should be more rapidly hydrolysed than its α-isomeride, and presumably, therefore, more rapidly formed. Applying these considerations to the preparation of methylfructoside by Fischer's method, the course of the reaction should be marked by first a decrease and then an increase of lævorotation; on hydrolysing the product, the reverse optical changes, namely, an increase and then a diminution of lævorotation, should be observed.

A solution of 20 grams of fructose in 188 c.c. of methyl alcohol containing 0·5 per cent. of hydrogen chloride was prepared according to Fischer's directions and kept at the ordinary temperature; polarimetric observations in a 2 dcm. tube were taken, at first every few minutes, and afterwards at longer intervals. As the solution gradually became yellow in colour, incandescent gas light was used throughout. A very rapid fall of rotation set in immediately on the solution being made up, which became gradually slower until a minimum was reached. This diminution of lævorotation was followed by a much slower increase, until the rotation became almost constant at approximately its original value. On now heating the solution at

35°, a second less extensive and very slow diminution of lævorotation occurred. The following observations may be recorded in illustration:

Condensation.

Time after solution.	Observed rotation $l=2$.
4 minutes	$-11{\cdot}92°$
15 ,,	8·99
24 ,,	6·69
2 hours 40 ,,	1·48
3 ,, 50 ,,	0·99
7 ,,	1·32
54 ,,	5·43
190 ,,	12·06
214 ,,	12·29

Time of heating at 35°.	Observed rotation $l=2$.
4½ hours	$-11{\cdot}18°$
16½ ,,	9·09
35½ ,,	8·20
39 ,,	8·08

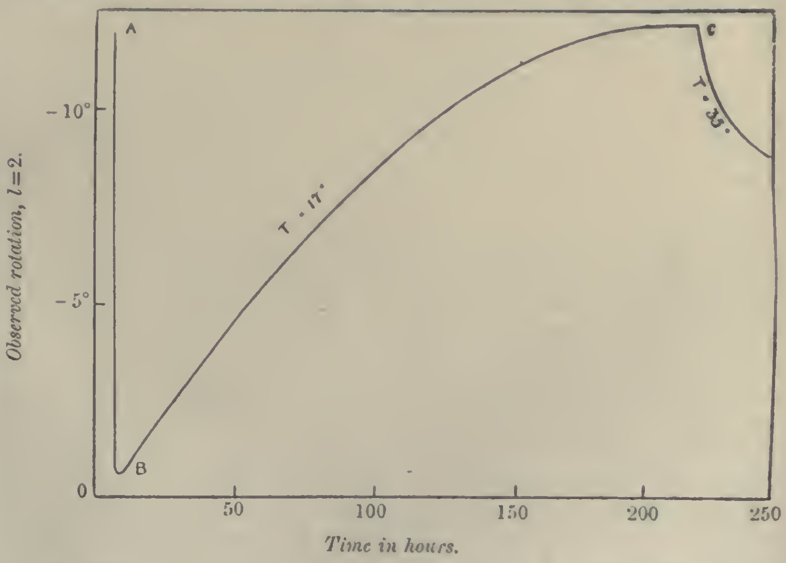
Hydrolysis.

Time after solution.	Observed rotation $l=2$.
4 minutes	$-4{\cdot}40°$
5 hours	6·05
21½ ,,	7·05
28½ ,,	7·04
44 ,,	6·60
166 ,,	6·01
238 ,,	6·01

Time of heating at 35°.	Observed rotation $l=2$.
20 hours	$-6{\cdot}55°$
40 ,,	7·01
64 ,,	7·29

The extensive diminution and subsequent increase of lævorotation during the condensation at the ordinary temperature accord with the conclusions indicated above. The smaller final decrease of rotation at higher temperature may be attributable to the condensing effect of

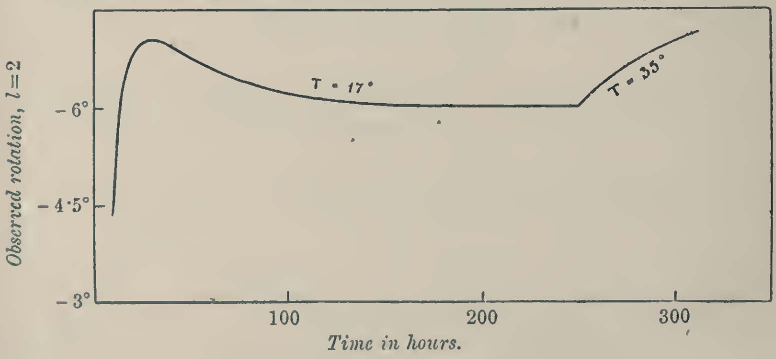
Curve showing optical changes during condensation of fructose with methyl alcohol.



hydrogen chloride on unaltered fructose, or, as suggested by later observations, to the partial conversion of the fructoside into a less lævorotatory isomeric hexoside. The first observation recorded (*A* on the curve), $\alpha - 11{\cdot}92°$ gives $[\alpha]_{\text{Auer}} - 56°$, which approximates to the specific rotation found for a solution of similar strength in pure methyl alcohol $[\alpha]^{20}_{\text{D}} - 57{\cdot}6°$. The minimum rotation, $(B) - 0{\cdot}99°$, indicates that β-methylfructoside is feebly lævorotatory, or possibly dextrorotatory. The subsequent maximum rotation, $(C) - 12{\cdot}29°$, probably marks an equilibrium between the two fructosides.

To observe the changes of rotation occurring during hydrolysis, the methylfructoside was procured in the syrupy state, as Fischer describes (*loc. cit.*) and dried in an exhausted desiccator. The specific rotation of the syrup in methyl alcohol ($c = 6{\cdot}466$) was $[\alpha]_{\text{Auer}} - 36{\cdot}6°$, a value approximating to that calculated from the final observation quoted above, namely, $-35{\cdot}2°$ ($\alpha - 8{\cdot}08°$, $c = 11{\cdot}465$, calculated as methylfructoside).

Curve showing reverse optical changes during hydrolysis of methylfructoside.



The specific rotation of the syrup in water ($c = 12{\cdot}867$) was $[\alpha]_{\text{Auer}} - 34{\cdot}3°$. This solution, after being diluted with an equal volume of water containing 4 per cent. of hydrogen chloride, was left to hydrolyse at the ordinary temperature and finally heated at 35°. Some of the observations made are recorded above.

In qualitative correspondence with the three changes of rotation occurring during the formation of the fructoside mixture, three oppositely directed changes of rotation occur during its hydrolysis. This is seen by comparison of the two curves which represent the optical changes occurring during the formation and hydrolysis respectively of the methylfructoside mixture. The observations, therefore, furnish evidence in support of the view that the mixture contains the two methylfructosides and a third hydrolysable product. The possibility of the presence of an acetal is, however, not excluded.

Methylation of Methylfructoside.

This process was carried out precisely as described in previous papers on the alkylation of aldosides. The proportion of the alkylating agents used and the method of isolating the product were also the same (Trans., 1904, **85**, 1074). The action proceeded in a similar manner, and oxidation did not appear to occur to any considerable extent. The yield of methylated product obtained on distillation was, however, less than in the case of the aldosides, amounting to only about a third of the weight of fructose originally taken. Thus, in one preparation, the methylfructoside from 60 grams of fructose gave on alkylation only 19 grams of crude distillate boiling at 130—150° under 16—18 mm. pressure; the remainder of the material could not be distilled without decomposition. This residue did not consist of incompletely alkylated fructoside, as, although readily soluble in methyl iodide, further treatment with the alkylating agents failed to render it capable of being distilled. The crude distillate referred to reduced Fehling's solution slightly, and had a distinctly acid reaction. To remove the acid impurity the substance was dissolved in ether and treated with barium carbonate. After drying the filtered solution with anhydrous sodium sulphate, removing the ether, and repeatedly distilling the residue, a neutral syrup, without action on Fehling's solution, was obtained. Two separate preparations boiling at 132—136° under 10 mm. and 140—146° under 17 mm. pressure respectively gave on analysis:

I. C = 52·86; H = 8·91; OMe = 61·1.
II. C = 52·84; H = 8·77; OMe = 59·7.
$C_6H_7O(OMe)_5$ requires C = 52·80; H = 8·80; OMe = 62·0 per cent.

The substance has, therefore, the composition of a tetramethyl methylfructoside.

It was found that much fractionation could be avoided and a much better yield obtained by the following distinct method of preparation. The crude product of the methylation of methylfructoside, without being previously distilled, was directly hydrolysed with dilute hydrochloric acid, as described later; the methylated reducing sugar so obtained was then remethylated by the silver oxide process, and the resulting liquid finally distilled. By this procedure, starting with 70 grams of fructose, 39 grams of distillate were collected (b. p. 136—146°), of which 24 grams boiled at 139—141° under 12 mm. pressure. The substance had no action on Fehling's solution, and its analysis gave figures similar to those already quoted.

III. C = 52·65; H = 8·70; OMe = 61·3.

The molecular weight in benzene solution by the cryoscopic method was found to be 230, the calculated number being 250.

The specific rotations in ethyl alcohol of the three specimens of the methylated fructoside, analyses of which are recorded above, were $[\alpha]_D^{20°}$ I – 15·6°; II – 18·8°; – 19·8°. These figures, in view of the difficulties of the preparation and the different methods employed, are fairly concordant, but the examination of a fourth specimen from a larger preparation carried out in the same manner as I and II showed that the substance was in fact not homogeneous in respect of rotatory power. Three fractions were collected on distillation boiling at 132°, 132—140°, and 140—150° under 16—18 mm.; the specific rotations of these determined as above were respectively + 1·2°, – 14°, and – 43·2°. The three fractions reacted slightly acid, but they reduced Fehling's solution only to a very slight extent even on boiling, and the figures obtained on analysis of each fraction approximated to those already quoted. The variation in rotatory power, which is too great to be accounted for by the traces of impurity indicated by the analyses, is discussed in the sequel.

Hydrolysis of Tetramethyl Methylfructoside.

This process was carried out by heating a 5 per cent. solution of the fructoside in 5 per cent. aqueous hydrochloric acid at 100° for about half an hour. The product was isolated as in previous cases (*loc. cit.*) and distilled. The substance thus obtained was a colourless neutral syrup which reduced warm Fehling's solution vigorously. After repeated distillation a fraction boiling at 142—146° under 14 mm. pressure gave on analysis:

$C = 50·60$; $H = 8·36$; $OMe = 50·3$.

$C_6H_8O_2(OMe)_4$ requires $C = 50·88$; $H = 8·56$; $OMe = 52·5$ per cent.

The substance has therefore the composition of tetramethyl fructose.

The rotatory power observed in a 2-dcm. tube was as follows:

In water ($c = 5·1405$), $[\alpha]_D^{20} - 18·1° \longrightarrow - 20·9°$.

In ethyl alcohol ($c = 5·1005$), $[\alpha]_D^{20} - 13·9° \longrightarrow 20·2°$.

The mutarotation indicated above was accelerated in the case of the alcohol solution by adding a trace of alcoholic ammonia, and the permanent stage was reached only after three and a half days. In aqueous solution the rotation became permanent in three hours, and remained so on adding a trace of ammonia. The alcoholic solution was made up immediately after the substance was distilled; the aqueous solution later; hence probably the difference in the range of the mutarotation in the two cases. The permanent specific rotations observed on two other preparations in alcoholic solution were – 21·7° ($c = 4·47$), and – 25° ($c = 5·28$), the initial rotation in the latter case being – 18°. It will be seen that the mutarotation observed is in the opposite sense to that exhibited by the parent sugar. This apparent anomaly is explained later.

It has been repeatedly shown in previous papers that the mixture of stereoisomeric alkylated aldosides, prepared from alkylated aldoses by the silver oxide process, contains the more readily hydrolysable β-isomeride in such large proportion that its presence can be detected by a diminution and subsequent increase of rotatory power during hydrolysis. This method of ascertaining the presence of two isomeric ketosides was accordingly applied to specimens of tetramethyl methylfructoside prepared by the two distinct processes already described.

A 4·5 per cent. solution, in 5 per cent. aqueous hydrochloric acid, of the substance obtained by the direct methylation of methylfructoside, was heated at 100°, and polarimetric observations were taken every ten minutes in a 2-dcm. tube, using a Welsbach light. The initial specific rotation, $[\alpha]_{\mathrm{Auer}}$ $-32{\cdot}7°$, diminished until after forty minutes it had attained the constant value, $-21{\cdot}2°$, or $-22{\cdot}5°$ calculating on the assumption that the methylated fructoside was entirely hydrolysed to tetramethyl fructose. This value agrees approximately with the values given above for the isolated product. The decrease of rotation was uniform, showing no such fluctuations as were recorded in hydrolysing the methylfructoside from which the substance was prepared.

A similar experiment was made with the tetramethyl methylfructoside obtained from tetramethyl fructose by the silver oxide process. The observations were made on a solution of the fructoside ($c = 5{\cdot}332$) in 2·5 per cent. aqueous hydrochloric acid which was heated in a thermostat at 50°. The initial specific rotation, $[\alpha]_{\mathrm{Auer}}$ $-38{\cdot}2°$, diminished until after four hours it had attained nearly the same constant value as before, $-23{\cdot}2°$, or, calculated for tetramethyl fructose, $-24{\cdot}5°$. The observations, therefore, furnish no evidence of the presence in either specimen of isomeric fructosides which differ widely in rotatory power and rate of hydrolysis.

Crystalline Tetramethyl Fructose.

A specimen of the distilled syrupy tetramethyl fructose described in the last section eventually showed signs of crystallisation. The available material, 17 grams in all, was accordingly nucleated and left to crystallise. By draining the resulting semi-solid mass on a porous plate and recrystallising repeatedly from light petroleum, 4 grams of pure substance were obtained in square plates, which melted sharply at 98—99°. Analysis gave:

$C = 50{\cdot}46$; $H = 8{\cdot}72$; $OMe = 52{\cdot}44$.

$C_6H_8O_2(OMe)_4$ requires $C = 50{\cdot}88$; $H = 8{\cdot}56$; $OMe = 52{\cdot}54$ per cent.

The molecular weight found in aqueous solution by the cryoscopic method was 218, the calculated number for tetramethyl fructose being 236. The compound was therefore identical in composition and molecular weight with the syrup from which it was obtained. It was very soluble in water and all organic solvents, except light petroleum, in which it dissolved sparingly. It acted vigorously on slightly warmed Fehling's solution. Being readily recovered in the crystalline state from its solutions, the material at our disposal, although small, sufficed for the observations recorded below.

From the analogy of tetramethyl glucose (Trans., 1904, 85, 1052) crystallisation from light petroleum should give the stable tetramethyl α-fructose, showing in solution, like crystallised fructose, a downward mutarotation. On heating this for some time above its melting point and rapidly cooling, the sugar should then contain a considerable proportion of the unstable β-form, which should be detected, if present in sufficient quantity, by mutarotation in the opposite sense. The observations tabulated below confirm these conclusions.

To obtain a solution in which the β-form should be in excess of the proportion contained in the equilibrium mixture, the sugar, immediately before making up the solution, was heated for two hours at 115—120°, and then solidified by cooling. The mutarotation was observed in approximately 5 per cent. solutions, a 2-dcm. tube being used.

	After recrystallisation from light petroleum. $[\alpha]_D^{20}$.		After heating for two hours at 115—120°. $[\alpha]_D^{20}$.	
Solvent.	Initial.	Final.	Initial.	Final.
Ethyl alcohol	−94·2°	−86·7°	−70·9°	−87·0°
Methyl alcohol............	99·0	95·6	—	—
Water	124·7	121·3	112·4	121·0

The oppositely directed mutarotations, it will be seen, reach approximately the same final values in similar solutions. The mutarotation in water was much more rapid than in the other solvents. The two upward changes of rotation in water and ethyl alcohol required two hours and seventy-nine hours respectively for completion. The rotatory power, as in the case of fructose, is higher in water than in the alcoholic solvents. In view of the observations here recorded, the apparently anomalous mutarotation of the syrupy tetramethyl fructose previously referred to finds ready explanation. The liquid having been recently distilled, it contained a larger proportion of the β-form than is present when equilibrium is reached in solution.

With the view of obtaining evidence of the production of α- and β fructosides when the crystalline hexose is methylated, the compound was reconverted into tetramethyl methylfructoside by the silver oxide process and also by Fischer's method. The two products were then separately hydrolysed and the course of the action followed by means of the polarimeter, as in similar experiments described in the last section.

Two grams of the ketose were used for methylation by the silver oxide process. The distilled liquid product, weighing 1·3 gram, was too small in quantity to be purified. Its fructoside nature was, however, evinced by the absence of action on Fehling's solution, and its composition approximated to that of tetramethyl methylfructoside. Analysis gave:

C = 52·15 ; H = 8·92.

$C_6H_7O(OMe)_5$ requires C = 52·80 ; H = 8·80 per cent.

Its specific rotation in ethyl alcoholic solution ($c = 5·03$) was $[\alpha]_D^{20}$ − 103·2°. The substance was hydrolysed by heating a solution of it ($c = 2·88$) in 2·5 per cent. hydrochloric acid at 50°. The specific rotation, however, contrary to expectation, did not increase and then decrease to approximately the value for tetramethyl fructose, but diminished uniformly during the process from $[\alpha]_{Auer}$ − 114·7° to − 100·2°, or, calculating the concentration for the theoretical yield of tetramethyl fructose, to − 106·1°. That the ketose had been produced by the hydrolysis was proved, however, by its recovery in the crystalline state from the product.

For methylation by Fischer's process, 1 gram of the crystalline ketose was used. The condensation proceeded rapidly at 50°, the specific rotation of the solution increasing uniformly during the process from − 97·7° to the constant value, − 135·6°. The isolated syrupy product had no action on Fehling's solution. On hydrolysis, under the conditions indicated above, the specific rotation decreased uniformly to the value recorded in the parallel experiment, namely, to − 106·2°. In this case also the product of the hydrolysis yielded the crystalline ketose. The final rotations reached on completion of the hydrolyses were less than the value for tetramethyl fructose, − 121·3°, but this is probably attributable to a secondary action of the hydrogen chloride on the sugar.

On adding a solution of phenylhydrazine acetate to tetramethyl fructose an oil is quickly deposited. This oil, after being washed with water, has no action on Fehling's solution even on boiling, but on treatment with hydrochloric acid and subsequent neutralisation the product shows distinct reducing action. An alcoholic solution of the oil is dextrorotatory; on adding aqueous hydrochloric acid the solution gradually becomes lævorotatory, and simultaneously acquires reducing power. The oil could not be crystallised, but from these observations it is doubtless a hydrazone.

Discussion of Results.

The results of previous researches show that the alkylation of the alcoholic hydroxyl groups of aldoses does not produce any striking change in their rotatory powers. Thus, for example, the specific rotation of α-glucose is +106°, that of tetramethyl α-glucose +101°. This statement also holds true in the case of fructose. The initial specific rotation of crystalline tetramethyl fructose in water is about −124°, that of the parent ketose about −104°. Fructose, like other reducing sugars, is, no doubt, capable of assuming two stereoisomeric forms of the γ-oxidic type, and, according to the now generally accepted view, the downward mutarotation of ordinary α-fructose implies a partial transformation into the less lævorotatory β-form. This form has, however, not been isolated, nor has a solid mixture of the two forms been obtained which in solution shows the oppositely directed mutarotation due to the change $\beta \longrightarrow \alpha$. In the case of tetramethyl fructose, on the other hand, a solid mixture of this kind is readily obtained from the α-form by fusion as already described. Evidence is thus furnished of the existence of both forms of this sugar in the solid state.

With respect to alkylfructosides, neither the α- nor the β-form of methylfructoside has as yet been isolated, but the changes of rotatory power which we observed during the production and hydrolysis of Fischer's substance are probably attributable to its being a mixture of the two stereoisomerides. In the case of tetramethyl methylfructoside no similar fluctuation of rotatory power was observed during its production from the syrupy or from the crystalline tetramethyl fructose by condensation with methyl alcohol. Observations on the change of rotatory power occurring during hydrolysis also failed to indicate the presence of stereoisomeric forms which hydrolyse at different rates. In every case, whether the compound was prepared from methylfructoside by direct alkylation, or from the syrupy or crystalline tetramethyl fructose by Fischer's process, or by the silver oxide process, its hydrolysis was accompanied by a uniform diminution of rotatory power. The failure to detect the more easily hydrolysable β-form by an initial rise of rotation during the reaction may be accounted for either by its not being present in sufficient quantity or, more probably, by the rotatory powers of the two isomerides not being sufficiently wide apart.

The relative rotatory powers of the fructosides obtained from crystalline tetramethyl fructose by the two methods ($[\alpha]_D^{20}$ −135·6° and −103·2° in alcoholic solution) are, however, in accord with previous experience of similarly prepared aldosides. The product of the silver oxide process is the less lævorotatory, and contains therefore the β-isomeride in larger proportion.

The rotatory powers of the tetramethyl methylfructoside mixtures, which were obtained by direct methylation of methylfructoside, varied considerably, but were in every case much lower than the values just quoted for the fructosides prepared from crystalline tetramethyl fructose. This cannot be accounted for by the former containing the β-form in larger proportion, as the syrupy ketose obtained from them and the ketoside mixtures prepared in turn from this ketose also showed correspondingly low lævorotations. We attribute the anomaly to the presence of dextrorotatory hexosides in the mixtures in question, which owed their origin to the occurrence of isomeric change during the preparation of the original methylfructoside. Irvine and Cameron (Trans., 1905, 87, 907) encountered a similar anomaly in the preparation of tetramethyl methylgalactoside and tetramethyl galactose from a syrupy mixture of methylgalactosides. Our supposition is borne out by the following observations. The original methylfructoside syrup showed an abnormally low rotatory power, $[\alpha]_{Auer}$ $-34\cdot3°$, in aqueous solution, and the lævorotation of the product of its hydrolysis was much less than that of fructose. It was also previously mentioned that, on distilling one of the preparations of tetramethyl methylfructoside, a small slightly lower boiling fraction was collected which possessed a feeble dextrorotation. Further, a dextrorotatory compound, probably a tetramethyl hexose, was found to be present in the syrupy mother liquor of the crystalline tetramethyl fructose. On recovering this syrup from the porous porcelain in which it was absorbed and distilling it, a fraction collected at 140° under 16 mm. pressure showed the specific rotation $+4°$.

We propose making a further study of the composition of the methylfructoside mixture which results from Fischer's method of condensation.

CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

XXXII.—*Studies on Optically Active Carbimides. Part V. The Aryl Esters and the Amides of* l-*Menthylcarbamic Acid.*

By Robert Howson Pickard and William Oswald Littlebury.

In Part II. (Trans., 1906, **89**, 94) it was shown that *l*-menthylcarbimide reacts very readily with alcohols, forming stable esters of *l*-menthylcarbamic acid. The most striking property of these esters is the regularity exhibited by the molecular rotations in various solvents; for example, in chloroform, the molecular rotations approximate to −160° and in pyridine to −175°. It appeared desirable to investigate this point further, and therefore we have determined the rotations of eleven aryl esters and eighteen amides of *l*-menthylcarbamic acid. The results may be summarised as follows: the approximately constant molecular rotation of −160° given in chloroform solution by the alkyl esters is also given by the aryl esters, the amide, and also such mono-substituted amides of *l*-menthylcarbamic acid as were prepared from a primary aliphatic amine, whilst the mono-substituted amides containing an aromatic radicle have a higher rotation.

Contrasted with the results obtained in chloroform solution, the molecular rotations of these compounds in pyridine solution are peculiar. Thus the aryl esters have molecular rotations approximating to −190°, that is, higher than the rotations of the alkyl esters, which approximate to −175°. This difference is doubtless due to the influence of the aromatic radicles, which is again observable in the rotations of the amides; for the mono-substituted *l*-menthylcarbamides with aliphatic substituents give values for the molecular rotation in pyridine which approximate to −160° (the value also given in chloroform solution), whilst those with aromatic substituents give much higher values. It is noteworthy that the two amides prepared from secondary amines, namely, diethylamine and piperidine, have comparatively high rotations in both solvents. The rotations of the amides have also been determined in absolute ethyl alcohol for the purpose of comparison with the rotations of the amides of *d*-butylcarbamic acid (Urban, *Arch. Pharm.*, 1904, **242**, 51). The effect of a varying substituent R in the amides of *d*-butylcarbamic acid, $C_4H_9 \cdot NH \cdot CO \cdot NHR$, is very much greater than in the amides of *l*-menthylcarbamic acid.

In view of the similarity in the constitution of menthylamine and menthol, it is interesting to compare the regularities in the molecular rotations in chloroform solution of the compounds described below and the numerous menthyl esters of aliphatic and aromatic acids described by Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606). These derivatives of the two parent substances owe their optical activity to the same complex, and certain regularities are to be observed in each series of compounds. Thus in the homologous series of the alkyl esters and amides of *l*-menthylcarbamic acid and in the *l*-menthyl esters of the homologous aliphatic acids there is an approximation to a constant value of the molecular rotation. It seems that in the complex containing the three asymmetric carbon atoms of menthol and menthylamine the optical activity is not altered merely by an alteration in the mass of the substituent in the hydroxyl or amino-group respectively, and even, with aliphatic substituents, by an alteration in the character of the substituents. Thus, for example, *n*-propyl-, cetyl-, and *iso*butyl-*l*-menthylcarbamates and the symmetrical ethyl-, allyl-, and *iso*butyl-*l*-menthylcarbamides all have about the same molecular rotation; and again *l*-menthyl propionate, *n*-nonate, and *iso*butyrate, for example, have the same molecular rotation; further, the constant rotation of − 160° given by the carbamates and carbamides in chloroform solution closely approximates to the rotation of − 158° given by the *l*-menthyl esters which were examined by Tschugaeff (*loc. cit.*) in the liquid state; whilst Wallach and Binz (*Annalen*, 1893, **276**, 317) have shown that the molecular rotations in chloroform solution of the *l*-menthylamides of acetic, propionic, and *n*-butyric acids all approximate to − 161°. The arrangement of the atoms in the menthyl radicle is therefore such that the optical activity to which it gives rise is affected, not by the mass, but only in some cases by the aromatic character of the groups to which the menthyl radicle is attached.

Now the introduction of an aryl radicle in the series of *l*-menthyl carbamides has much the same influence on the rotation in chloroform solution that it has on the rotations of *l*-menthyl esters of aromatic acids as compared with those of the esters of aliphatic acids. Aryl substituents in these compounds cause very well-marked and variable alterations in the rotations, and therefore it is remarkable that the aryl esters of *l*-menthylcarbamic acid, like the alphyl esters, such as the benzyl, phenylethyl, cinnamyl, and phenylpropyl esters (Part II, *loc. cit.*), all give in chloroform solution molecular rotations approximating to − 160°.

Among the smaller differences in the molecular rotations it may be noted (I) that among the aryl esters and amides of *l*-menthylcarbamic acid the compounds containing the following radicles: *o*-tolyl, phenyl, *m*-tolyl, *p*-tolyl have molecular rotations increasing in the order given, thus agreeing with the rule on the influence of these substituents on the rotation of organic compounds as laid down by Frankland and Wharton (Trans., 1896, **69**, 1320 and 1583) and confirmed by Guye and Babel (*Arch. Sci. Phys. Nat.*, [iv], 7, 109), and (II) that among the aryl esters the influence of the radicles 1 : 2 : 5-xylenyl, 1 : 2 : 4-xylenyl and 1 : 3 : 4-xylenyl is to increase slightly the molecular rotation in the order given, which is the same as found by Cohen and Briggs (Trans., 1903, **83**, 1214) in their investigation of the *l*-menthyl esters of the various dichlorobenzoic acids.

EXPERIMENTAL.

Aryl Esters of l-*Menthylcarbamic Acid.*

Two methods have been employed for the preparation of the aryl esters of *l*-menthylcarbamic acid. The simpler, but more expensive, is to treat the phenols with *l*-menthylcarbimide, the alternative method being to allow the aryl esters of chlorocarbonic acid dissolved in light petroleum to react with *l*-menthylamine in the presence of sodium hydrogen carbonate. Both methods give products of the same rotation, thus affording additional evidence that no racemisation takes place during the preparation of the carbimide (see Part I, Trans., 1904, **85**, 688).

Of the esters described below the 1 : 3 : 4-xylenyl, 1 : 2 : 5-xylenyl, 1-naphthyl and 2-naphthyl were prepared only by the first method, molecular proportions of the phenol and carbimide being heated in a sealed tube for about thirty hours at 100—110° until the mixture became quite solid when cold.

The aryl esters of chlorocarbonic acid, $Cl\cdot CO_2R$, were prepared by shaking a solution of carbonyl chloride in toluene with a solution of the phenol in aqueous caustic soda and were purified by distillation under reduced pressure, which allows of an easy separation from the small quantities of the carbonates formed in the above reaction. They were all obtained as colourless mobile liquids, highly refractive, and having penetrating odours. The following table shows their boiling points:

Phenylchlorocarbonate	boils at		97°	under	25 mm.
o-Tolyl	,,	,,	110—120°	,,	28 ,,
m-Tolyl	,,	,,	103°	,,	22 ,,
p-Tolyl	,,	,,	108°	,,	30 ,,
1 : 2 : 4-Xylenyl	,,	,,	126—128°	,,	25 ,,
Thymyl	,,	,,	129°	,,	25 ,,
Carvacryl	,,	,,	135—137°	,,	25 ,,

The aryl esters of *l*-menthylcarbamic acid, $C_{10}H_{19}\cdot NH\cdot CO_2R$, are all colourless compounds crystallising readily from dilute alcohol or from light petroleum. They are not volatile with steam, and are readily soluble in chloroform or pyridine, but sparingly so in benzene.

Aryl Esters of l-*Menthylcarbamic Acid.*

					Analysis.	
Ester.	Empirical formula.	Crystalline form.	Solvent.	M. p.	N found.	Theory per cent.
Phenyl…………	$C_{17}H_{25}O_2N$	Prismatic needles	Dilute alcohol	138°	4·9	5·1
o-Tolyl…………	$C_{18}H_{27}O_2N$	Silky needles	Dilute alcohol	148	5·0	4·8
m-Tolyl ………	$C_{18}H_{27}O_2N$	Silky needles	Light petroleum	100	5·2	4·8
p-Tolyl…………	$C_{18}H_{27}O_2N$	Needles	Light petroleum	119	5·1	4·8
1 : 3 : 4-Xylenyl	$C_{19}H_{29}O_2N$	Flat needles	Dilute alcohol	104	4·6	4·6
1 : 2 : 4-Xylenyl	$C_{19}H_{29}O_2N$	Silky needles	Light petroleum	137	4·4	4·6
1 : 2 : 5-Xylenyl	$C_{19}H_{29}O_2N$	Prismatic needles	Dilute alcohol	135	4·8	4·6
Thymyl ………	$C_{21}H_{33}O_2N$	Prismatic needles	Light petroleum	129	4·5	4·3
Carvacryl………	$C_{21}H_{33}O_2N$	Prismatic needles	Light petroleum	149	4·4	4·3
1-Naphthyl……	$C_{21}H_{27}O_2N$	Silky needles	Alcohol	163	4·3	4·3
2-Naphthyl……	$C_{21}H_{27}O_2N$	Small prisms	Dilute alcohol	120	4·6	4·3

Rotation of the Aryl l-*Menthylcarbamates.*

The rotations recorded in this paper have been determined in a 2-dcm. tube at temperatures between 18° and 20°. It was found that such small variations in the temperature and a variation in the concentration between 2 and 5·5 parts per 100 of solution have no appreciable effect on the rotation.

Rotations in Chloroform.

Ester.	Weight in grams.	Volume of solution in c.c.	Observed rotation.	$[\alpha]_D$.	$[M]_D$.
Phenyl ………………	1·0460	20	− 6·04°	− 57·83°	159·0
o-Tolyl ………………	0·8128	20	4·45	54·74	158·2
m-Tolyl………………	0·9433	20	5·27	55·86	161·4
p-Tolyl ………………	0·6840	20	3·85	56·28	162·6
1 : 3 : 4-Xylenyl ……	0·6043	20	3·23	53·45	161·9
1 : 2 : 4-Xylenyl ……	0·7162	20	3·68	51·38	155·7
1 : 2 : 5-Xylenyl … ..	0·4350	20	2·22	51·30	154·6
Thymyl………………	1·0442	20	4·75	45·48	150·5
Carvacryl ……………	0·6295	20	3·23	46·64	154·5
1-Naphthyl …………	0·9063	20	4·67	51·52	167·4
2-Naphthyl .. ………	0·8515	20	4·10	48·15	156·5

Rotations in Pyridine.

Ester.	Weight in grams.	Volume of solution in c.c.	Observed rotation.	[α]D.	[M]D.
Phenyl	1·0384	20	−7·00°	−67·41°	185·4°
o-Tolyl	0·8343	20	5·38	64·48	186·3
m-Tolyl................	1·1392	20	7·54	66·17	191·2
p-Tolyl	0·7481	20	4·85	64·82	187·3
1 : 3 : 4-Xylenyl	0·7885	20	4·98	63·16	191·4
1 : 2 : 4-Xylenyl	0·5595	20	3·46	61·84	187·3
1 : 2 : 5-Xylenyl	0·4677	20	2·94	62·86	190·4
Thymyl................	0·9433	20	5·31	56·29	186·3
Carvacryl	0·6234	20	3·59	57·58	190·6
1-Naphthyl	0·9992	20	6·34	63·45	206·2
2-Naphthyl	1·0400	20	6·23	59·90	194·6

The Amides of l-*Menthylcarbamic Acid*, $C_{10}H_{19}\cdot NH\cdot CO\cdot NHR$.

With the exception of the unsubstituted amide, *l*-menthylcarbamide, the amides are readily obtained by the action of the carbimide on the amines. With aliphatic amines it is necessary to moderate the violence of the reaction by diluting the reagents with light petroleum, whilst with the aromatic amines gentle warming is sometimes necessary to complete the reaction.

l-*Menthylcarbamide* was prepared from potassium cyanate and *l*-menthylamine hydrochloride according to the directions of Wallach (*Annalen*, 1898, **300**, 279).

Phenyl-l-*menthylcarbamide* prepared from *l*-menthylcarbimide and aniline is identical in properties with the compound obtained by Wallach (*loc. cit.*) by the action of phenylcarbimide on *l*-menthylamine.

Amides of l-*Menthylcarbamic Acid.*

					Analysis.	
Amide.	Empirical formula.	Crystalline form.	Solvent.	M. p.	N found.	Theory per cent.
Ethyl	$C_{13}H_{26}ON_2$	Stout prisms	Dilute alcohol	114°	12·5	12·4
n-Propyl	$C_{14}H_{28}ON_2$	Stout prisms	Dilute alcohol	100	11·7	11·7
n-Butyl	$C_{15}H_{30}ON_2$	Prismatic needles	Aqueous acetone	61	10·9	11·0
*iso*Propyl	$C_{14}H_{28}ON_2$	Long prismatic needles	Dilute alcohol	146	12·0	11·7
*iso*Butyl	$C_{15}H_{30}ON_2$	Small prismatic needles	Aqueous acetone	80	11·3	11·0
tert.-Butyl * ...	$C_{15}H_{30}ON_2$	Long prismatic needles	Dilute alcohol	223	11·3	11·0
Allyl	$C_{14}H_{26}ON_2$	Prismatic needles	Dilute alcohol	115	11·9	11·8

* Only sparingly soluble in chloroform or pyridine.

Amides of l-*Menthylcarbamic Acid* (continued).

Amide.	Empirical formula.	Crystalline form.	Solvent.	M. p.	Analysis. N found.	Analysis. Theory per cent.
Diethyl	$C_{15}H_{30}ON_2$	Transparent hairy stellate needles	Dilute alcohol	142°	10·9	11·0
Benzyl............	$C_{18}H_{28}ON_2$	Micro-crystalline mass	Dilute alcohol	158–159	9·9	9·7
o-Tolyl	$C_{18}H_{28}ON_2$	Slender needles	Dilute alcohol	201	9·4	9·7
m-Tolyl *	$C_{18}H_{28}ON_2$	Long silky needles	Alcohol	197	9·7	9·7
p-Tolyl	$C_{18}H_{28}ON_2$	Small needles	Alcohol	179–180	9·6	9·7
1-Naphthyl * ...	$C_{21}H_{28}ON_2$	Needles	Alcohol	242	8·7	8·6
2-Naphthyl ...	$C_{21}H_{28}ON_2$	Small needles	Acetic acid	200	8·8	8·6
Pentamethylene (piperidyl)	$C_{16}H_{30}ON_2$	Small needles	Alcohol	169	10·5	10·5

* Almost insoluble in chloroform.

Rotations of the Carbamides.

In Chloroform Solution.

Symmetrical menthyl carbamides. $C_{10}H_{19}\cdot NH\cdot CO\cdot NHR$.	Weight in grams.	Volume of solution in c.c.	Observed rotation.	$[\alpha]_D$.	$[M]_D$.
Ethyl	0·6187	19·9	−4·30°	−69·16°	156·3°
n-Propyl...............	0·6105	19·9	4·05	66·03	158·4
n-Butyl	0·6142	19·9	3·86	62·55	158·9
*iso*Propyl	0·6609	19·9	4·30	64·76	155·4
*iso*Butyl...............	0·5534	19·85	3·54	63·51	161·3
tert.-Butyl	0·6201	50	1·68	67·72	172·0
Allyl	0·6475	19·9	4·25	65·33	155·5
Benzyl	0·4060	19·9	2·10	51·47	148·3
Phenyl	0·3672	19·8	2·58	69·68	191·0
o-Tolyl	0·4141	25	1·86	56·14	161·7
p-Tolyl	0·3283	25	1·79	68·15	196·3
2-Naphthyl	0·1983	20	1·31	66·06	214·7
$C_{10}H_{19}\cdot NH\cdot CO\cdot NR''$.					
Diethyl	0·6428	19·9	5·08	78·66	199·8
Pentamethylene ...	0·3979	20	3·23	81·17	215·9
Monomenthylcarbamide...............	0·5195	19·85	4·21	80·44	159·3
* Dimenthylcarbamide	0·5698	19·9	5·15	89·93	302·1

* Part I (*loc. cit.*).

Solutions in Pyridine.

Symmetrical menthyl carbamides. $C_{10}H_{19}$·NH·CO·NHR.	Weight in grams.	Volume of solution in c.c.	Observed rotation.	$[\alpha]_D$.	$[M]_D$.
Ethyl	0·5739	19·9	−4·05°	−70·23°	158·7°
n-Propyl	0·6385	19·9	4·29	66·88	160·5
n-Butyl	0·6061	19·85	3·92	64·19	163·0
*iso*Propyl	0·6240	19·85	4·10	65·22	156·5
*iso*Butyl	0·5571	20·1	3·55	64·03	162·7
tert.-Butyl	0·6154	50	1·63	66·21	168·2
Allyl	0·6463	19·85	4·43	68·05	161·9
Benzyl	0·3914	19·9	2·33	59·26	170·7
Phenyl	0·5854	19·9	4·79	81·41	223·1
o-Tolyl	0·4773	19·9	3·66	76·29	219·8
m-Tolyl	0·4412	20	3·60	81·59	235·1
p-Tolyl	0·5631	20	4·57	81·15	233·7
1-Naphthyl	0·2649	25	1·49	70·31	228·6
2-Naphthyl	0·3322	20	2·61	78·56	255·4
$C_{10}H_{19}$·NH·CO·NR″.					
Diethyl	0·6153	19·9	4·61	74·56	189·3
Pentamethylene ...	0·3805	19·9	2·99	78·18	208·0
Monomenthylcarbamide............	0·5331	19·9	4·13	77·11	152·7
Dimenthylcarbamide	1·2391	20	11·88	95·87	322·1

*Solutions in Ethyl Alcohol.**

Symmetrical menthyl carbamides. $C_{10}H_{19}$·NH·CO·NHR.	Weight in grams.	Volume of solution in c.c.	Observed rotation.	$[\alpha]_D$.	$[M]_D$.
Ethyl	0·6206	19·9	−4·60°	−73·77°	166·7°
n-Propyl	0·6149	19·9	4·33	70·08	168·2
n-Butyl	0·6071	19·9	4·05	66·39	168·6
*iso*Propyl	0·6199	19·9	4·20	67·42	161·8
*iso*Butyl	0·6126	19·9	4·11	66·76	169·5
tert.-Butyl	0·6941	19·85	4·53	64·77	164·5
Allyl	0·6188	19·9	4·31	70·11	166·9
Benzyl	0·4292	19·9	2·45	56·80	163·6
Phenyl	0·5820	19·9	4·58	78·32	214·6
o-Tolyl	0·5264	19·9	3·49	65·98	190·0
m-Tolyl	0·5561	50	1·68	75·51	217·5
p-Tolyl	0·5701	19·9	4·31	85·23	245·5
2-Naphthyl	0·3780	25	2·15	71·09	231·1
$C_{10}H_{19}$·NH·CO·NR″.					
Diethyl	0·6348	19·9	4·80	75·25	191·1
Pentamethylene ...	0·5309	19·9	4·61	86·42	229·9
Monomenthylcarbamide............	0·5093	19·9	4·18	81·87	162·1
Dimenthylcarbamide	0·5056	19·85	5·02	98·56	331·1

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* Pure ethyl alcohol, free from aldehydes, which was dried over baryta until crystal of potassium permanganate produced no pink coloration.

We desire to express our thanks to Mr. Allen Neville, B.Sc., who prepared five of the carbamides described, and to the Research Fund Committee of the Society for a grant which has defrayed some of the cost of the material for this work.

Municipal Technical School,
Blackburn.

XXXIII.—*Note on the Arsenates of Lead and Calcium.*

By Spencer U. Pickering, M.A., F.R.S.

As an insecticide for leaf-eating insects, lead arsenate has lately come into general use, since it does not scorch foliage in the same way as does Paris green or London purple. It is made by precipitating sodium arsenate with the acetate or nitrate of lead; but, unfortunately, so many different instructions have been issued by various authorities, both in this and other countries, as to the proper proportion in which these reagents should be used, that the matter has been reduced to a state of confusion. This is all the more to be regretted, as excess of the soluble arsenate, and, to a lesser extent, excess of the lead salts, is injurious to foliage.

Some account of an investigation on this subject has been published in the Sixth Report of the Woburn Experimental Fruit Farm, 1906, p. 157, but the details of the chemical facts established may be more appropriately recorded here.

The sodium arsenate listed by manufacturers, either without specification, or as "pure," "cryst," or "hydrated," is the disodium orthoarsenate, generally containing 7 molecules of water of crystallisation, but, occasionally, 12. In the case of four samples out of five which were obtained from different manufacturers, the salt was found to be the heptahydrate; in the fifth, it was dodecahydrate. Determinations of the water contents by prolonged drying at 100°—the results of which are given in Table I, Col. II, samples A to E—indicated that these samples all attained a high standard of commercial purity, although they differed from each other slightly in alkalinity. Sample X was one which was prepared by careful recrystallisation.

As the values in the table imply, the whole of the water of crystallisation may be driven off at 100°, although it is generally stated that a temperature of 200° is necessary for this purpose, and even 300°, according to the British Pharmacopœia, 1898, should be employed. When the crystallised salt is allowed to fuse during dehydration, there is considerable difficulty in driving off all the water at 100°, but, if it is partially desiccated before being heated, no such difficulty is experienced. On further heating to 150°, it begins to change into the pyroarsenate, and this change is rapid at 300°. The theoretical loss of water in the conversion of $Na_2HAsO_4,7H_2O$ into $Na_4As_2O_7$ is 43·30 per cent.; the values found with sample X at 300° were 43·21 and 43·17. No fusion occurs if the hydrated arsenate is dehydrated slowly. Thus, the temperature for drying prescribed in the British Pharmacopœia is much too high, and the only sample of this medicinal arsenate which was examined was found, in consequence, to consist mainly of pyroarsenate, instead of orthoarsenate.

Table I.—*Precipitation of Sodium Arsenate by Crystallised Lead Acetate.*

		Weight of lead acetate required for 1 gram of			
				Na_2HAsO_4 present.*	
Arsenates. I.	Pure Cryst. Na_2HAsO_4. II.	The sample. III.	Hydrated arsenate present. IV.	Before heating. V.	After heating. VI.
“Pure hydrated” samples.					
Heptahydrates:					
Theory for $Na_2HAsO_4,7H_2O$ ..	**59·60**	—	**1·822**	**3·056**	—
X. (Recryst.)	59·75	1·823	1·846	3·098	3·116
	59·68	1·853	1·876	3·149	2·958
A	59·41	1·696	1·703	2·854	—
B	59·79	1·739	1·724	2·917	—
C	59·84	1·761	1·768	2·943	—
D	59·24	1·798	1·787	3·035	—
Mean	59·62	1·779	1·784	2·999	—
Dodecahydrate:					
Theory for $Na_2HAsO_4,12H_2O$.	**46·27**	—	**1·414**	**3·056**	—
E	46·48	1·389	1·383	2·987	—
“Pure anhydrous” samples.					
Theory for Na_2HAsO_4	**100·00**	—	—	**3·056**	—
F. (Fused)	101·53	3·014	—	2·966	—
G. (Exsic. B. P.)	102·96	3·194	—	3·102	—
“Crude anhydrous” samples..					
H	103·31	2·583	—	2·500	2·601
I	101·38	2·539	—	2·505	2·538
J	92·33	3·027	—	3·278	3·237
K	86·76	2·757	—	3·180	3·316
Theory for $Na_4As_2O_7$	**105·09**	—	—	**3·212**	—

* Or its equivalent of $Na_4As_2O_7$.

In the earlier determinations, which were published in the Report of the Woburn Experimental Fruit Farm, some of the samples used were overheated in drying, and the water contents, consequently, appear too high. The values have been corrected for this error in the present communication, or fresh determinations have been substituted for them.

The amount of crystallised lead acetate required for the precipitation of 1 gram of the various samples of sodium arsenate was determined by running a standard solution of the acetate into a solution of the arsenate. Filtration was necessary after each addition. The final reaction is not very clearly marked, lead arsenate not being a very insoluble substance; duplicate determinations, however, never differed by more than 1 or 2 per cent. of the total.

The results of the precipitation are given in Table I. These show that the lead arsenate precipitated must be the triplumbic salt. The equation $2Na_2HAsO_4 + 3Pb(C_2H_3O_2)_2,3H_2O = Pb_3(AsO_4)_2 + 2C_2H_4O_2 +$ &c. requires 3·056 parts of lead acetate for one part of anhydrous arsenate present, and the mean of the values found with the various samples is 2·999 (Col. V). This is the reaction which had been accepted as correct in Canada and the United States. According to it, for one part of the heptahydrated and dodecahydrated arsenate 1·822 or 1·414 parts, respectively, of lead acetate would be required. The Board of Agriculture and Fisheries (Leaflets 4, 20, 62, and 69) recommends the use of three parts of lead acetate to every one part of crystallised sodium arsenate; this would, obviously, give an unnecessary, and, as I have shown elsewhere, an injurious excess of lead salt. The use of two parts of acetate to every one part of crystallised arsenate would be amply sufficient to ensure the precipitation of all the arsenate in every case.

The reaction is the same whether the acetate is added to the arsenate, as above, or *vice versâ*. Thus, with the samples A and C the values obtained on adding acetate to arsenate were 2·854 and 3·095; mean, 2·915; and on adding arsenate to acetate, 2·912 and 3·074; mean, 2·943. A similar identity of results was obtained with various samples of crude arsenate.

The results with two "pure anhydrous" samples are next given in the table. Sample G is that prepared by drying at about 300°, and sold as "Exsic. B.P., 1898"; the other is sold as "fused," and is prepared at a somewhat lower temperature. Both of these samples, on redrying at 300°, lost less water than they should have done if they had consisted of the orthoarsenate, and, consequently, the arsenic acid present in them represents more than 100 per cent. of orthoarsenate; they were, however, not entirely in the condition of pyroarsenate, as 100 parts of this represent 105·09 parts of orthoarsenate, and 102·96 was the highest value found. The results obtained on precipitating this sample with lead acetate give a value (3·194) approximating that required by the pyroarsenate, which is 3·212.

Some samples of "crude anhydrous" sodium arsenate were examined, in order to ascertain how much lead acetate would be required in practice for their precipitation. It will be seen from the water determinations, that two of these appeared to consist partially of the pyroarsenate; the other two contained a notable amount of water. The latter, J and K, give values, on precipitation (Col. V), agreeing fairly well with the results with pure samples, although both are somewhat high, this, no doubt, being due to the presence of an excess of arsenic acid; for all the samples the crude arsenates gave an acid, instead of an alkaline, reaction. The other two samples, H and I, gave values too low to be reconcilable with the action being the same as in other cases. With both of them the lead acetate required was 2·5 parts to every one of $Na_2H(AsO_4)$ present, and this proportion agrees well with that required if the lead arsenate precipitated were a mixture of equal molecular proportions of $Pb_3(AsO_4)_2$ and $Pb_2H_4(AsO_4)_2$, the calculated requirement in such a case being 2·546. Further reference to this point will be made below.

It will be seen that another set of values for the lead acetate required for precipitation are given in the last column of the table. These apply to samples of the arsenate after they had been heated to 300°. They were made because some previous determinations—those published in the Report of the Woburn Experimental Fruit Farm—had indicated that a higher lead value was obtained after the sample had been heated, suggesting that the pyroarsenate formed by the heating of the salt remained as such when dissolved in water (like a pyrophosphate), and reacted with the lead acetate in a manner different from the orthoarsenate. The present determinations do show a difference in the lead values in this same direction, but it is too small to be of any significance, especially as similar determinations with the pure arsenate, X, showed no such difference, the mean of the duplicate values in that case (Cols. V and VI) being 3·124 and 3·087, before and after heating, respectively.

For practical purposes it would not be safe to take less than 3·5 parts of lead acetate for 1 part of crude arsenate if the precipitation of all the arsenate is to be ensured, although, often, a good deal less might suffice (see Col. III).

On examining the same samples of sodium arsenate by precipitation with lead nitrate, instead of with lead acetate, it was evident that a different reaction occurred. The values given by the five hydrated samples (Table II) give, as a mean, 1·743 parts of nitrate to every 1 of anhydrous arsenate present in them. This indicates that the arsenate formed must be the diplumbic ($PbHAsO_4$), and not the triplumbic salt, since the formation of the latter would necessitate the use of 2·669 parts of the nitrate, whereas that of the former requires 1·780 parts. The values in the individual cases are not very concordant, but they leave no doubt as to the general nature of the reaction, although the diplumbic salt formed may be mixed in some cases with a certain amount of the triplumbic salt, and, in others, with some of the monoplumbic salt. The variations in the values are not, however, due to chance circumstances, such as temperature or the proportion of the water present; for duplicates wherein these circumstances were varied did not show differences of more than 2 per cent., whereas the differences observed in the table extend to 10 per cent.; they can, therefore, be accounted for only by differences in the nature of the different samples, and it will be noticed that the three commercial samples which required the largest amount of lead nitrate—C, D, and E—are the same which required the largest amount of lead acetate.

TABLE II.—*Precipitation of Sodium Arsenate by Lead Nitrate.*

	Weight of lead nitrate required for 1 gram of		
Arsenate.	The sample.	Hydrated arsenate present.	Na_2HAsO_4 present.
"Pure hydrated" samples.			
Heptahydrates:			
Theory for $Na_2HAsO_4,7H_2O$ ... If $PbHAsO_4$ formed	—	**1·061**	**1·780**
X. (Recryst.)	1·084	1·096	1·839
A	1·005	1·008	1·691
B	0·902	0·899	1·509
C	1·092	1·096	1·822
D	1·097	1·095	1·855
Mean	1·036	1·038	1·743
Dodecahydrate:			
Theory for Na_2HAsO_4,H_2O	—	**0·823**	**1·780**
E	0·900	0·896	1·936
"Pure anhydrous" samples.			
Theory for Na_2HAsO_4:			
If $Pb_3(AsO_4)_2$ formed	—	—	**2·669**
If $Pb_5H_2(AsO_4)_4$ formed ...	—	—	**2·224**
If $PbHAsO_4$,, ...	—	—	**1·780**
If $PbH_4(AsO_4)_2$,, ...	—	—	**0·890**
F. (Fused)	1·922	—	1·894
G. (Exsic. B. P.)	1·896	—	1·889
"Crude anhydrous" samples.			
H	1·946	—	1·883
I	2·150	—	2·121
J	2·257	—	2·447
K	2·210	—	2·547

With the two "pure anhydrous" samples, F and G, the lead nitrate required is, on the average, somewhat greater, and it is even slightly greater than what would be required if the sodium arsenate were present entirely as the pyro-salt, for the pyro-salt requires only 1·870 parts of lead nitrate, whereas the samples in question took about 1·9 parts. But the end reaction in the case of precipitation with lead nitrate, is less well marked than where the acetate is used, and the values, consequently, are less certain. The diplumbic arsenate appears to be more soluble than the triplumbic salt, and, before the whole of the arsenic acid is precipitated, some excess of lead nitrate must be added. A mixture of the two reagents may be obtained, in which turbidity will be caused by the addition of more of either of them.

Determinations with the samples of the crude sodium arsenate are also given. The amount of lead nitrate required by these varies considerably, and in two cases, J and K, it is nearly equivalent to that required for the formation of the triplumbic salt. With sample H, the diplumbic salt was precipitated, as in the case of the samples of pure arsenate, whilst with the sample I we get a value intermediate between the di- and triplumbic salts.

Mr. F. J. Smith (*Ann. Rep. Mass. Board of Agriculture, and Ann. Rep. of the Hatch exp. Station of Mass. Agri. Coll.*, 1897, 357) gives the reaction between sodium arsenate and lead nitrate as resulting in the formation of a mixture, or compound, of the triplumbic and diplumbic arsenates in equivalent proportions, $Pb_3(AsO_4)_2 + Pb_2H_2(AsO_4)_2$, or $Pb_5H_2(AsO_4)_4$. Such an arsenate might very conceivably exist, either as a molecular compound or otherwise; but it seems evident that the lead arsenate formed—at any rate when the materials are pure—is simply the diplumbic salt, and it is only with one sample out of the twelve here examined (and that a sample of crude arsenate, I), that a value was obtained agreeing fairly with the formation of the complex arsenate—2·121 against 2·224; at the same time, it may be observed, the values obtained by precipitation with lead acetate indicated, both in the case of this sample and in that of H, the formation of the same complex lead arsenate. It is clear, however, that we cannot establish the correctness of a chemical reaction, and, still less, the existence of a new salt, on the strength of determinations with crude and obviously very impure substances. Whether Mr. Smith's results were based on the examination of crude samples, and what value he attached to his equation, as representing an actual reaction, or merely as indicating the proportions required in practice, I am unable to determine, as I have been unable to obtain a copy of his paper, and my information on the subject is derived from Dr. Felt, State Entomologist to the United States. An abstract of Mr. Smith's paper will be found in the Experimental Station Records, 1899, p. 567, but it gives no information on the point in question.

As with lead acetate, so with the nitrate, it appears that the reaction with sodium arsenate is substantially the same, whether the lead salt is added to the arsenate, or *vice versâ*. Three of the samples of arsenate gave the following values for the lead nitrate required to precipitate one part of anhydrous arsenate present in them :

	When nitrate is added to arsenate.	When arsenate is added to nitrate.
Sample A (pure)	1·691	1·679
,, J (crude)...............	2·447	2·407
,, K (,,)...............	2·547	2·196

Whichever reagent is added to the other, some excess of it will be required before precipitation is complete ; when, therefore, the lead nitrate is added to the arsenate, the amount of it required will appear greater than when the process is reversed ; the difference, however, is not great, except in the case of the sample K.

In order to ensure the precipitation of the whole of the arsenate when lead nitrate is used as the precipitant, I should recommend that in practice 1¼ parts of it be used for every one part of crystallised sodium arsenate, or 2¼ parts for every one part of crude arsenate.

Calcium Arsenate.

It is probable that the lead in lead arsenate is of little or no value for insecticidal purposes, and that the cheaper calcium arsenate would be equally effective, if it were suitable in other respects ; indeed, it has already been used for this purpose in the United States. A brief note of the chemical facts elucidated in the examination of calcium arsenate will be sufficient.

When calcium nitrate or calcium chloride is added to sodium arsenate, a bulky flocculent precipitate is gradually formed, and at the same time minute crystals are deposited on the side of the vessel. The weight of precipitate formed, when increasing amounts of the calcium salt are added to an equivalent of sodium arsenate, increases until 1½ equivalents of the calcium salt is reached, but increases no further with any excess of the latter up to 4½ equivalents. This shows that the calcium arsenate which separates, is the tricalcium salt, the reaction for its formation requiring 1½ equivalents of calcium to one of sodium arsenate. The calcium arsenate, however, is far from being very insoluble, and the amount precipitated does not approach the total amount formed, unless the liquid is concentrated. With 1 gram of hydrated sodium arsenate, and a total volume of 100 c.c. of liquid, the calcium arsenate precipitated amounts to only one-third of the calculated amount, and if the total volume is 300 c.c. no precipitate at all is formed. Judging by these results, the solubility of calcium arsenate should be about 1 in 200, and an arsenate of this solubility would be useless for spraying trees, owing to the scorching effect which it would have on the foliage.

In the presence of lime, however, the whole of the calcium arsenate is precipitated from the solution. Thus, when lime water is added to sodium arsenate, no arsenate remains in solution so long as the proportion of lime added is slightly in excess of 1½ equivalents to 1 equivalent of the arsenate. Here, again, it is evidently the tricalcium arsenate which is formed. The precipitate when first thrown down is bulky, flocculent, and opaque, but it soon shrinks and clots together, becoming more transparent and semi-crystalline. Its condition then is not such as would render it suitable for use in a spraying machine.

By using milk of lime, however, and keeping the lime in considerable excess, a mixture is obtained which would appear quite manageable for spraying purposes. Using pure lime, it was found that about three equivalents to every one of arsenate are sufficient to insure the precipitation of the whole of the arsenic acid, the excess of calcium salt in this case being necessitated by the particles of lime becoming coated with arsenate, and being thus prevented from becoming easily available for the reaction. In practice, where an impure lime would be used, it would be advisable to increase the proportions of lime still further, say, to double the amount mentioned above, which would mean mixing equal weights of lime and crystallised sodium arsenate.

XXXIV.—*The Absorption Spectra of Phthalic,* iso-*Phthalic, and Terephthalic Acids, Phthalic Anhydride, and Phthalimide.*

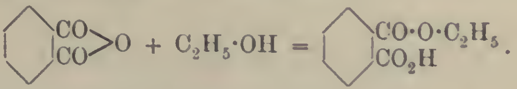
By WALTER NOEL HARTLEY and EDGAR PERCY HEDLEY.

PHTHALIC acid was examined by Hartley and Huntington (*Phil. Trans.*, 1879, 170, I, 257), and the diagram showing the nature of the absorption is placed next to that of benzoic acid, on Plate 28 of that paper. As, however, the other acids isomeric with phthalic acid have not been examined, it was considered desirable that information concerning them should be supplied. It was thought probable that *iso-* and tere-phthalic acids would each show an absorption similar to that of the *o*-acid, with this difference, that the *p*-compound would show a more persistent band or a broad absorption. On comparing the curves of the three acids, it will be seen that our preconceived ideas have not been realised. The *o*-phthalic acid gives a well-defined broad band, the *m*-acid only a shallow band, the portion of its head being in the same region as that of the *o*-acid, but the *p*-compound gives no band whatever, merely a sudden extension in the region of the band of the other two acids.

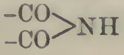
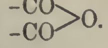
Some difficulty occurred with terephthalic acid arising out of its sparing solubility, so that it was found impossible to dissolve 1 milligram-molecule in 100 c.c. of the solvent. Accordingly the dimethyl ester was prepared and its absorption photographed instead of that of the acid.

On comparing the curve of benzoic acid with that of phthalic acid, it will be seen that the latter gives a wider band, which was to be expected.

Phthalimide and phthalic anhydride were dissolved in cold absolute alcohol and their spectra photographed. The former exhibited a spectrum with great general absorption and a band of great width and persistency. When boiled for an hour and again examined, the spectrum was absolutely the same. Phthalic anhydride exerts only a general absorption of considerable magnitude, but on warming the solution for only five or six minutes to 60° a remarkable change is made evident; the general absorption has decreased and the sudden extension of the transmitted rays indicates the formation of an absorption band being in progress. After boiling for twenty minutes another series of photographs was taken, which showed that a remarkable change had taken place; the general absorption had enormously decreased and a well-defined absorption band had appeared, the whole spectrum resembling almost exactly that of phthalic acid. Though this point has not yet been definitely decided, there can be but little doubt that the mono-ester was formed, thus:



On continuous boiling for an hour no further change occurred in the spectrum.

When the results obtained with phthalimide and phthalic anhydride are compared, it appears that the group  $\begin{matrix}-CO\\-CO\end{matrix}\!\!>\!NH$ is more stable than  $\begin{matrix}-CO\\-CO\end{matrix}\!\!>\!O$.

EXPERIMENTAL.

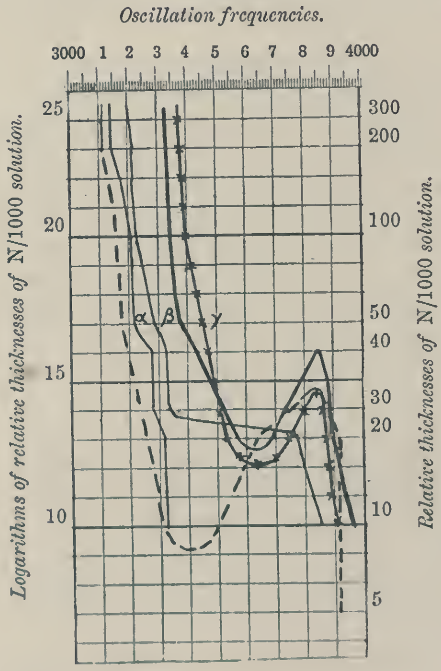
All the compounds, which for the most part were obtained from Kahlbaum, were very carefully purified before use.

The Phthalic Acids.—These were recrystallised. The phthalic acid melted at 213°. The *iso*-acid had no definite melting point, but the temperature of liquefaction was above 300°, whilst the dimethyl ester of the terephthalic acid melted at 140—141°.

The Potassium Salts of Phthalic Acids.

These were prepared by dissolving the acids in aqueous caustic potash and crystallising from water. They formed well-defined, colourless crystals. Their respective absorption curves are given in Figs. 2 and 3.

FIG. 1.



Phthalic acid ——
Phthalimide - - -
Phthalic anhydride, cold solution α: 1st light curve.
The same after warming β: 2nd light curve.
The same after boiling – × – × – × – γ.

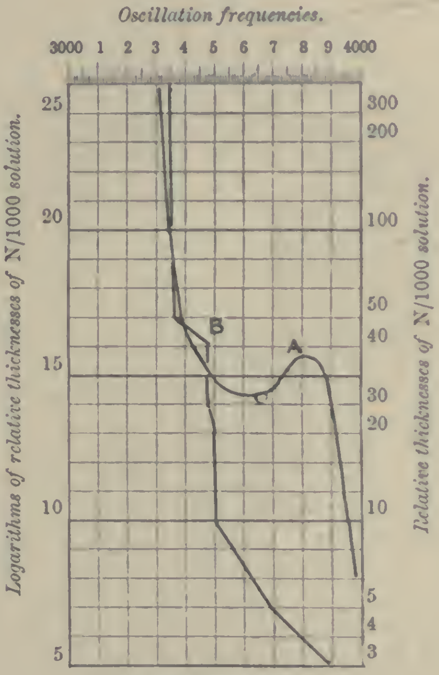
It is noticeable that the general absorption increases from the *o*-salt to the *p*-salt. The *o*-salt is the only one which gives a band, the head of which is almost in the same place as in the case of potassium and silver benzoates. There is a slight sudden extension in each of the other curves which indicates a band of like kind to that of the other salts of the acids.

Phthalic Anhydride.—This was obtained from Kahlbaum and recrystallised. It melted at 128°. The absorption curve is shown on Fig. 1.

Phthalimide.—This was obtained from Kahlbaum, and, when purified, melted at 238°. Its absorption curve on Fig. 1 will be seen to be twice as wide and persistent as that of phthalic anhydride.

Solutions of the substances containing 1 milligram-molecule in 100 c.c. of solvent were examined as a rule through a 3 mm. cell, and the characteristic absorption bands are recorded below :

FIG. 2.



A. iso*Phthalic acid.*
B. *Potassium* iso*phthalate.*

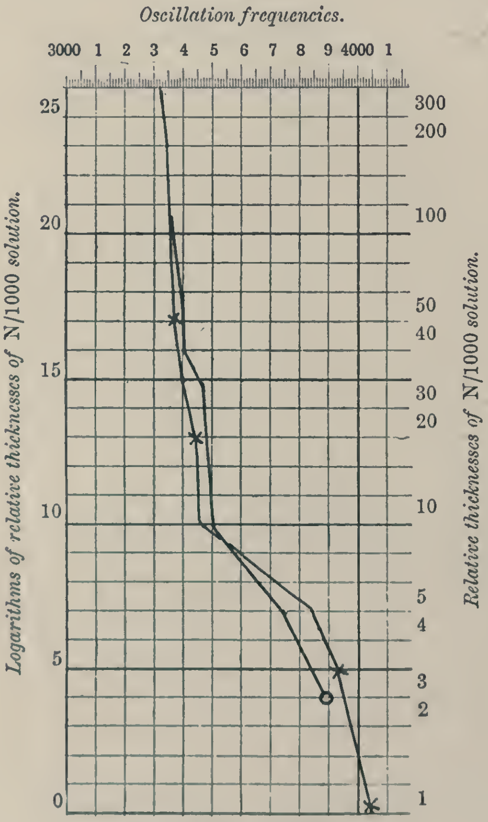
	Absorption bands.					
	λ.		λ.	$^1/\lambda$.		$^1/\lambda$.
Phthalic acid 1 : 2, in water	*2872*	to	*2659*	**3482**	to	**3760**
*iso*Phthalic acid 1 : 3, in alcohol...............	*2834*	,,	*2662*	**3528**	,,	**3756**
Potassium phthalate, water 2 mm............	*2829*	,,	*2768*	**3534**	,,	**3612**
Phthalimide, in alcohol..........................	*3105*	,,	*2616*	**3220**	,,	**3822**
Phthalic anhydride in alcohol, after boiling	*2876*	,,	*2626*	**3476**	,,	**3808**

It is particularly interesting to observe how clearly a change in constitution is shown when phthalic anhydride is dissolved first in cold absolute alcohol, then warmed to 60° for five minutes, and finally boiled.

Conclusions.

1. *o*-Phthalic acid gives an absorption curve of the character that might be expected from comparison with that of benzoic acid, and from the difference in constitution between benzoic and phthalic acids; that is to say, the curve begins in rays less refrangible than that of benzoic acid, and the absorption band is wider. *iso*-Phthalic acid has a shallow band of absorption situated in the same place as that of phthalic acid, but it is much less persistent. Judging from the dimethyl ester and the normal salts, terephthalic acid cannot

FIG. 3.



Potassium terephthalate, ○.
Dimethyl terephthalate, ×.

be said to show any band, but merely an extension of the transmitted rays at or near where a band might be expected.

2. In phthalimide the grouping $\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}\!\!>\!\mathrm{NH}$ has greater stability than the group $\begin{matrix}\mathrm{CO}\\\mathrm{CO}\end{matrix}\!\!>\!\mathrm{O}$ in phthalic anhydride.

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XXXV.—*The Absorption Spectra of Benzoic Acid, the Benzoates, and Benzamide.*

By WALTER NOEL HARTLEY and EDGAR PERCY HEDLEY.

THE absorption spectrum of benzoic acid has been photographed repeatedly, and has always been found to have a characteristic band which is situated between λ 280 and λ 270 with a continuous absorption beyond λ 255 (Kayser's *Handbuch der Spectroscopie*, **3**, 483, 1904). In an interesting communication made by Baly and Collie to the Society (Trans., 1905, **87**, 1332), it is stated: "The spectrum of benzoic acid has been observed by Hartley and Huntington (*Phil. Trans.*, 1879, **170**, i, 257), and only shows general absorption rather strongly. This is only to be expected from the presence of the ketonic oxygen in the *β*-position."

On referring to the diagram of the absorption spectra of benzoic acid at different dilutions in the last-mentioned paper, it will be seen that an absorption band is shown distinctly at a dilution of one part of the substance in 5000 parts of water or 1 gram in 5000 c.c. of alcohol, which becomes extinct with one part in 8000. Moreover, the adjoining diagram shows a similar band to occur in phthalic acid, but it lies more towards the red and is more persistent. In both instances the rays more refrangible than the absorption band are much weakened, and this is represented by a shading. The result of their examination of the absorption spectrum of benzoic acid led Baly and Collie to describe it as having no absorption band, and although such a difference in experimental results may possibly be explained by their use of the iron arc spectrum as a source of rays, and the band being feeble, it is rather difficult to accept their reason why the absence of such a band might be expected, inasmuch as such a band is characteristic of benzaldehyde (Hartley and Huntington, *Proc. Roy. Soc.*, 1880, **31**, 1; also Baly and Collie, *loc. cit.*, 1905).

The following benzoyl derivatives also show distinctly marked bands, the *syn-* and *anti*-benzaldoximes, dibenzoylmethane and α-hydroxybenzylideneacetophenone, and ethyl α-, β-, and γ-dibenzoylsuccinates (Hartley and Dobbie, Trans., 1900, **77**, 498). The curves of these esters, two of which were found to be absolutely identical, were drawn from the spectra photographed under different conditions, and what is of prime importance, the measurements of the spectra and especially of the bands were recorded. Baly and Desch (Trans., 1904, **85**, 1029) state that one of the three isomerides does not exhibit a band, but only a general absorption, and as this refers to the results in the paper quoted, it is surely a mistake. Again, as regards the dibenzoylmethane and α-hydroxybenzylideneacetophenone, it is said "these two compounds give spectra which appear somewhat similar, each having two absorption bands. The absorption bands of the one compound are sufficiently near in position to those of the other to justify the conclusion that the benzoylmethane was not entirely ketonic, and the α-hydroxybenzylideneacetophenone was not solely enolic." It is correct to say that the spectra are very similar and that they each have two bands; the smaller band in the more refrangible rays occupies very nearly the same position in each compound, but the more important and larger bands in the less refrangible rays are as wide apart as they well can be, considering that the substances are isomerides. In fact, the whole curve in the one case is shifted down into a region of less refrangible rays. To remove these discrepancies and uncertainties it has been deemed best to establish those points which are simple matters of fact, and to this end benzoic acid has been reinvestigated with some benzoates and benzamide.

A specimen of very carefully purified benzoic acid was dissolved in absolute alcohol, and a series of absorption spectra was photographed from it by the rays from the spark of a cadmium-tin and a cadmium-lead electrode, the source of radiations most generally employed (Hartley, *Phil. Trans.*, 1885, **176**, 471—521, "Absorption Spectra of the Alkaloids." Also *Journal of the Society of Arts*, 1886, **36**, 395; Proc., 1899, **15**, 47).

The cadmium in the two alloys has usually been reduced to 15 per cent., so that there was 85 per cent. of tin in the one electrode and 85 per cent. of lead in the other.

The band of absorption in the benzoic acid solution, although feeble, was distinctly marked. The observation was repeated on another plate and with another spectrograph with lenses of shorter focus; in fact, the absorption spectrum of benzoic acid has been, at various times since 1879 and under different conditions, photographed with lenses of 91 cm., 50 cm., and 35 cm. focus, and in all essential particulars the spectra showed no difference.

In the first case the photographs ranged from λ 4480 to λ 2145 and were 200 cm. in length; in the last they were 100 cm. The original photographs of Hartley and Huntington were taken with electrodes of cadmium only, but the result was the same.

Potassium and Silver Benzoates.

Aqueous solutions of beautifully crystallised silver and potassium salts were examined with electrodes of cadmium, and in each case a narrow absorption band was photographed. When instead of cadmium the electrodes were made from the alloys, the band was obscured by the strong metallic lines in the spectrum. Salts of some organic acids show wider and more intense bands than the acids themselves, but in this case the bands are narrower. To ascertain whether any change could be effected by adding an excess of alkali, four equivalents of caustic potash solution were added to a molecule of the potassium benzoate, but there was absolutely no difference to be observed between the neutral and alkaline solutions. Hence it is evident that the difference between the spectra of benzoic acid and its salts is not due to any isodynamic or tautomeric change, nor to hydrolysis, or ionisation of the salts. Independent observations were made by each of us on the absorption spectra of benzamide, and the results obtained were identical.

Benzamide shows an absorption curve with a band almost the same as that of silver benzoate. The solution of benzamide was made with alcohol, that of the benzoate with water, and the source of rays was the spark between cadmium electrodes only.

EXPERIMENTAL.

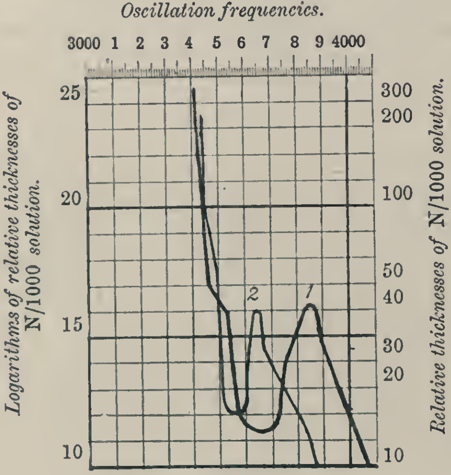
Benzoic Acid.—This was prepared from calcium benzoate by decomposing it with hydrochloric acid and recrystallising the product several times. It was obtained in beautiful long silky crystals which melted sharply at 122°.

Potassium and Silver Benzoates.—The salts were prepared with great care, the silver salt in particular; it was finely crystallised and almost white.

On comparing the curves it will be seen that they both commence at the same point, but the curve of the molecule of the light metal is long and the band narrow, whilst that of the salt of the heavy metal is shallow and the band broad. This recalls the spectra of the nitrates, where a similar difference is to be seen between the salts of potassium and silver (Trans., 1902, 81, 571).

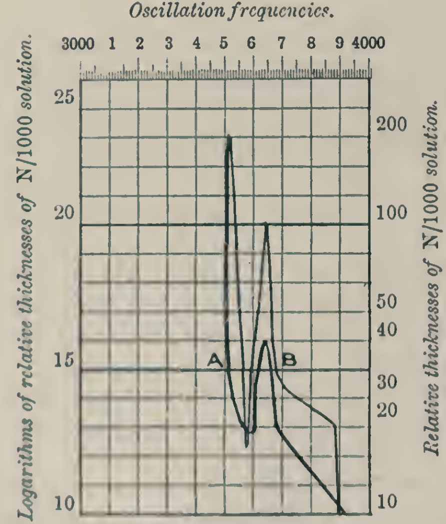
It is interesting to note that the heads of these two curves are in the

FIG. 1.



1. *Benzoic acid.*
2. *Benzamide.*

FIG. 2.



A. *Silver benzoate.*
B. *Potassium benzoate.*

same position as that of the first band of anisole and phenetole (Baly and Collie, *loc. cit.*).

At a uniform thickness of 3 mm. of solution containing 1 milligram-molecule of substance in 100 c.c. of solvent, the bands photographed gave the following measurements:

	Absorption bands.					
	λ.		λ.	$^1/λ$.		$^1/λ$.
Benzoic acid, in alcohol	*2824*	to	*2666*	**3540**	to	**3750**
Potassium benzoate, in water	*2806*	,,	*2777*	**3563**	,,	**3601**
Silver benzoate, ,, ...	*2842*	,,	*2768*	**3518**	,,	**3612**
Benzamide, in alcohol	*2842*	,,	*2768*	**3518**	,,	**3612**

Benzamide.—This was prepared by the action of benzoyl chloride on ammonia. It was well crystallised and melted at 128°.

Its absorption curve, Fig. 1, is almost identical with that of silver benzoate, Fig. 2. All the solutions were made so that one milligram-molecule of the substance was contained in 100 c.c. of alcohol or of water as the case might be, and where necessary the solutions were diluted ten times. It was found best to employ the cadmium electrodes only, for the benzoates and benzamide, but for the acid the alloys were satisfactory.

Conclusions.

(1) The original statement of Hartley and Huntington, that benzoic acid shows an absorption band, is confirmed as being correct, and the measurement of the band given in Kayser's *Handbuch der Spectroscopie*, as from λ 280 to λ 270, corresponds with the width of the band observed when a layer of 2 mm. of a solution is examined, containing 1 milligram-molecule of the substance in 100 c.c. of alcohol.

(2) Potassium and silver benzoates exhibit spectra with absorption bands which are both narrower than the band shown by the acid.

(3) Benzamide also shows an absorption band which bears a stronger resemblance to that of silver benzoate than to that of the acid itself or of potassium benzoate.

(4) Since a large excess of caustic alkali causes no alteration in the absorption curve of potassium benzoate, the band is proved to be due to the benzene ring.

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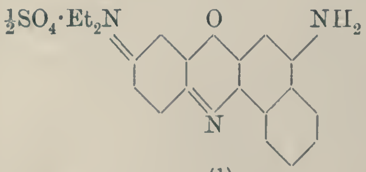
XXXVI.—*A Reaction of certain Colouring Matters of the Oxazine Series*

By JOCELYN FIELD THORPE.

DURING some experiments on the staining of pathological sections for the microscope, Professor Lorrain Smith and Dr. Powell White, of the Manchester University, made the discovery that certain blue colouring matters of the oxazine series, when used as a stain for sections containing neutral fat globules, possessed the remarkable property of colouring the fatty matter red, while, in the ordinary course, staining the protein matter blue. The two colouring matters of the series which they found exhibited this property most strongly were Nile-blue A (1) and New Methylene-blue GG (2), although Nile-blue BB (3) and Meldola's blue (4) also gave the same reaction after having been previously boiled with very dilute mineral acid.



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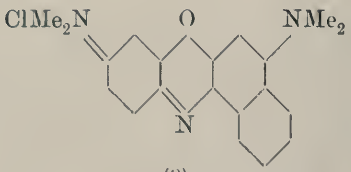

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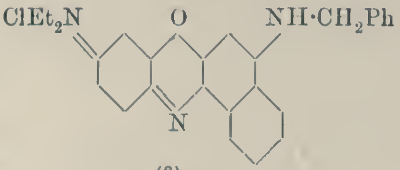

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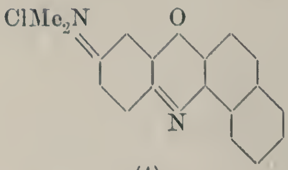
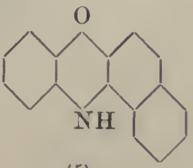


(4).

These gentlemen also found that the compound producing the red fat stain could be extracted from the blue solution of the colouring matter by means of xylene, in which it formed a red solution showing strong yellow fluorescence, and that after being completely extracted in this way more could be obtained on warming the dye solution with dilute hydrochloric or sulphuric acids. At their request I undertook to investigate the chemistry of this phenomenon.

Experiments with several typical dye-stuffs of the oxazine series showed at once that this reaction was exhibited only by those colouring matters which are derivatives of phenonaphthoxazine (5), and that those dyes which are derivatives of phenoxazine (6) were not capable of being converted into a red compound under the same experimental conditions.



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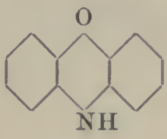
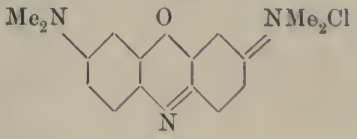


(6).

Thus the two Capri-blues GN (7) and GON (8) did not give this reaction, which was, however, exhibited by New-blue B (Cassella) (9),



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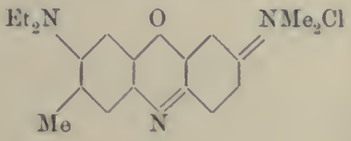

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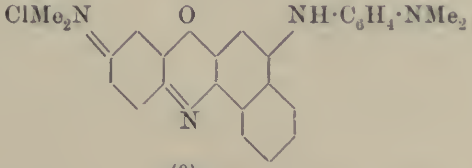

(9).

as well as by those colouring matters the formulæ of which are given on page 324. The oxazine colouring matters which are capable of being converted into a red compound can therefore be divided into two classes. (*a*) Those derivatives of phenonaphthoxazine which contain an amino- or substituted amino-group in the position 6.[*] (*b*) Those which have this position free. Of class (*a*), Nile-blue A (1), Nile-blue BB (3), New Methylene-blue GG (2), and New-blue (B) (9) are instances, whereas the only commercial colouring matter which falls into class (*b*) is Meldola's blue (4).

In the case of dye-stuffs of class (*a*), the production of the red compound is due to the replacement of the amino- or substituted amino-group by hydroxyl and the consequent formation by intermolecular change (see p. 331) of the corresponding phenonaphthoxazone. Thus Nile-blue A (1) and Nile-blue BB (3) are converted into 3-diethylaminophenonaphthoxazone (10), whereas New Methylene-blue GG (2) and New-blue B (9) are converted into 3-dimethylaminophenonaphthoxazone (11).

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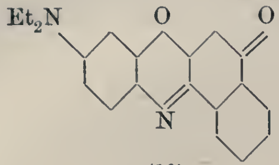
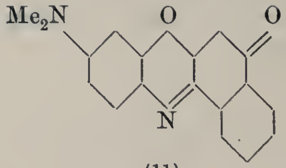
[*] The method of numbering is that recommended by Kehrmann and Gauhe (*Ber.* 1897, **30**, 2131).



(10).



(11).

Both these compounds have been prepared by Möhlau and Uhlmann, the former (*Annalen*, 1896, **289**, 124) by the interaction of nitrosodiethyl-*m*-aminophenol and α-naphthol, and the latter (*loc. cit.*, p. 126) from nitrosodimethyl-*m*-aminophenol and α-naphthol. The compounds prepared from the colouring matters mentioned above are identical with these substances described by Möhlau and Uhlmann.

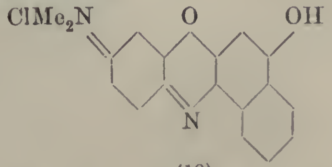
The rapidity with which the colouring matters of Class (*a*) are converted into the oxazones is dependent on the condition of the amino-group in the position 6. If this group is unsubstituted, as is the case in Nile-blue A (1), its replacement takes place remarkably quickly, and an aqueous solution of 3 grams of the blue can be completely converted into the oxazone on heating on the water-bath for twelve hours, provided that the solution is rendered slightly acid by means of dilute sulphuric acid and that it is covered with some suitable solvent such as xylene, which will extract the oxazone as soon as it is formed.

No trace of diethylaminophenonaphthoxazone (10) can be extracted from the solid colouring matter, and it is apparently first formed on dissolving the dye in water. The quantity, however, produced in this way is extremely small, but owing to the fluorescence exhibited by its solutions, its presence can be readily detected by shaking the dye solution with ether or xylene.

If the amino-group is substituted by alphyl groups, as is the case in New Methylene-blue (2), its replacement takes place almost as quickly as when it is unsubstituted. Thus a solution of 3 grams of New Methylene-blue can be completely converted into dimethylaminophenonaphthoxazone (11) on heating on the water-bath for fifteen hours, the conditions being the same as those indicated in the case of Nile-blue A. If, however, the amino-group is substituted by benzyl (Nile-blue BB) or by the dimethylaminophenyl group (New-blue B), its replacement takes place with much greater difficulty, and it is necessary to heat an acidified solution of the dye for several days before the whole of it will have been transformed into the oxazone.

Both dimethylaminophenonaphthoxazone (11) and diethylaminophenonaphthoxazone (10) form salts with hydrochloric acid containing one equivalent of the acid. These salts form deep blue stable solutions in hot dilute hydrochloric acid, but are dissociated by water.

It is probable therefore that they possess the formulæ (12) and (13) respectively,



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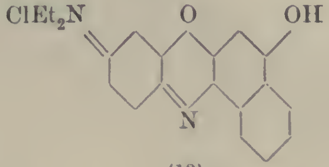
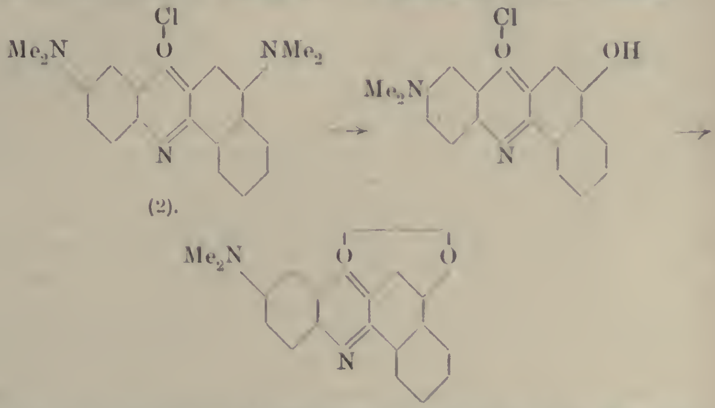


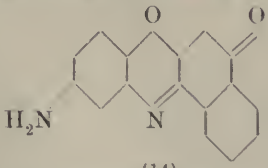
(13).

and that the passage of the salt to the base is accompanied by intermolecular rearrangement. In any case, if the *p*-quinone formula for these dyestuffs is correct, compounds of formulæ (12) and (13) must occur as intermediate products in the transformation of Nile-blue A and New Methylene-blue GG into the corresponding oxazones. If, however, the oxonium formula of Kehrmann is employed, the assumption of an intermolecular change is unnecessary. Thus, in the case of New Methylene-blue, the change can be represented by the formulæ



(2).

It should be mentioned, nevertheless, in connexion with this point, that 2-aminophenonaphthoxazone (14), which Kehrmann and Gauhe (*Ber.*, 1897, 30, 2132) prepared from the corresponding 2-nitro-derivative, and which is precluded from forming a *p*-quinone salt, although not from yielding a salt of oxonium, dissolves in dilute hydrochloric acid, forming a yellow solution,



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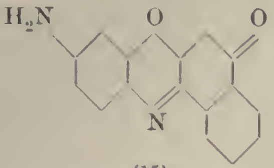


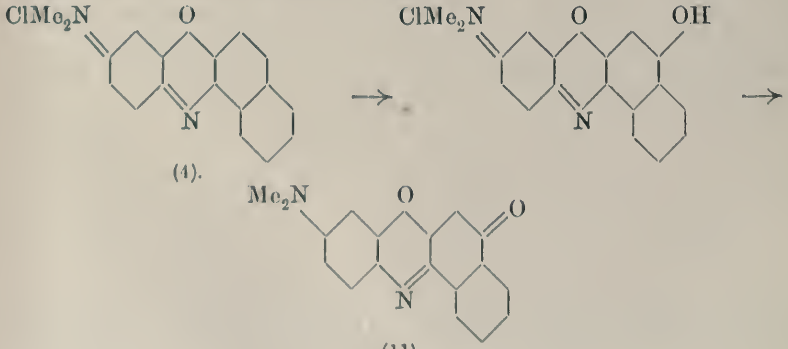
(15).

whereas 3-aminophenonaphthoxazone (15), also prepared by Kehrmann and Gauhe (*loc. cit.*, 2136), in which the formation of a *p*-quinone salt is possible, gives violet-blue solutions in dilute mineral acids, or, in other words, behaves in the same way as the 3-dialkylaminophenonaphthoxazones described above.

There can be no doubt that the blue salts of the dialkylaminophenonaphthoxazones remain dissolved in the dye solutions from which they are derived; at any rate, a considerable proportion of the oxazine colouring matter can be converted into the salt of the oxazone without any dissociation of this salt taking place. This can be readily shown by taking advantage of the fact that if wool is boiled in a hot acidified solution of the salt of the oxazone it is dyed a deep blue, which, owing to the decomposition of the salt on the fibre, is changed to red on washing with water. Nile-blue A can be boiled for a considerable time with dilute acid without any appreciable change in colour taking place, but if wool is dyed in the boiled solution of the blue, a dyed fabric will be obtained which will become markedly purple on washing with water; moreover, the presence of the oxazone in large amount in the boiled dye solution can be illustrated by the fact that when shaken with xylene the xylene solution becomes strongly fluorescent.

Xylene therefore has the power of extracting the weak oxazone base from a solution of its salt, and there can be no doubt that the mechanism of the reaction by which the neutral fat globules are stained red is of the same kind. The fat, in which the oxazone is readily soluble, extracts the base from the solution of its salt, becoming thereby coloured a brilliant red; at the same time the protein matter in the section is coloured blue by the excess of unchanged Nile-blue present.

The only commercial colouring matter belonging to Class (*b*) is Meldola's blue (4), which does not give the red fat stain until it has been boiled for some time with dilute acid. In this case also the compound producing the red stain can be extracted by means of xylene. When isolated, this substance was found to be identical with the compound produced from New Methylene-blue, or, in other words, to be 3-dimethylaminophenonaphthoxazone (11):



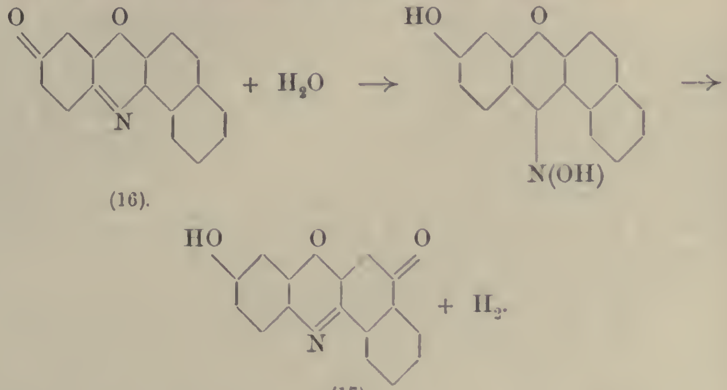
(4).

(11).

In this case, therefore, the entrance of an hydroxyl group has been caused to take place in the position 6.

On searching the literature for other instances of this rather remarkable reaction, it was found that Fischer and Hepp (*Ber.*, 1903, **36**, 1810) had recorded a similar reaction in the case of phenonaphthoxazone (16), which they found on boiling in alcoholic solution with hydrochloric acid to be partially transformed into 3-hydroxyphenonaphthoxazone (17).

They explain this reaction by assuming that water is first added on to the quinone ring, forming an oxime, from which the phenonaphthoxazone is produced by intermolecular change; the two superfluous hydrogen atoms being removed by the oxygen of the air thus:

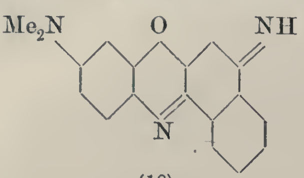


(16).

(17).

In the case of Meldola's blue it is probable that these hydrogen atoms reduce a portion of the colouring matter to its leuco-base. Strong evidence was obtained of the formation of this base, although it was not found possible to isolate it in a condition sufficiently pure for analysis. The leuco-base, however, readily oxidises in the air, regenerating the base of the colouring matter, and therefore if precautions are taken to allow of the free access of air from time to time during the course of the experiment, about 80 per cent. of a weighed quantity of Meldola's blue can be converted into the oxazone.

Möhlau and Uhlmann (*Annalen*, 1896, **289**, 120) prepared the base both of 3-dimethylaminophenonaphthoxazine chloride (Methyl Nile-blue) and of 3-diethylaminophenonaphthoxazine sulphate (Ethyl Nile-blue, Nile-blue A), and describe these compounds as forming strongly fluorescent solutions in organic solvents. These substances, which in their anhydrous state have the formulæ (18) and (19) respectively,



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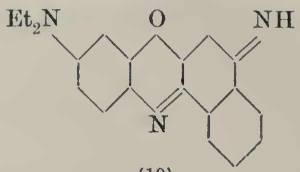

(19).

were prepared from the solution of the colouring matter by the action of caustic soda. The base of Nile-blue A according to my experiments does not form solutions which are fluorescent in ordinary daylight, and it is only when it is mixed with the corresponding oxazone that such fluorescent solutions are produced.

Experiments show that it is impossible to obtain the base of the colouring matter in the manner described by these chemists without it being mixed with varying quantities of the oxazone. Möhlau and Uhlmann obtained the base in pale brown needles from hot dilute alcohol, a process in itself probably sufficient to convert some of it into the oxazone. Moreover, they only estimated the percentage of carbon and hydrogen in their product, which, since the difference in the percentage of these elements in the oxazone and oxazine is within the limits of experimental error, is not sufficient to distinguish between them. A nitrogen determination would have indicated that they were working with a mixture of the two compounds.

That the base of Nile-blue A forms non-fluorescent solutions is shown by the following experiment. An acidified solution of the colouring matter was extracted with xylene until the extract ceased to be coloured, when it was cautiously treated with dilute caustic soda solution and again extracted with xylene. The insoluble base which was precipitated on the addition of the alkali dissolved in the xylene, imparting to it a deep red colour without fluorescence. The xylene solution was carefully dried and then concentrated by distillation, the residue after being freed from the remainder of the xylene on the water-bath being crystallised from benzene. The pale brown needles obtained in this way were dried at 100° to constant weight and analysed:

0·2307 gave 26·3 c.c. of nitrogen at 17° and 765 mm. $N = 13·43$.

$C_{20}H_{19}ON_3$ requires $N = 13·3$ per cent.

The base dissolves in most of the usual organic solvents, forming reddish solutions without fluorescence, all the other properties of the compound being the same as those described by Möhlau and Uhlmann. It differs from the oxazone in being completely extracted from its xylene solution by means of dilute hydrochloric acid, whereas a solution of the oxazone can be shaken with dilute acid without any of it being extracted. In this way the presence of the oxazone in the base prepared according to the directions of Möhlau and Uhlmann was established.

Formation of 3-Diethylaminophenonaphthoxazone from Nile-blue A and from Nile-blue 2B.

Nile-blue A.—In the first instance the solid commercial colouring matter was extracted with ether and with xylene. In both cases the solvent remained colourless, showing that the oxazone was not present; in order, however, to remove any impurities a quantity of the colouring matter was crystallised from water and the amount of nitrogen determined in the product:

0·2154 gave 19·6 c.c. of nitrogen at 17° and 770 mm. N = 11·63.
$(C_{20}H_{20}ON_3)_2,SO_4$ requires N = 11·5 per cent.

Three grams of the purified dye were dissolved in 500 c.c. of water contained in a large flask, 3 c.c. of concentrated sulphuric acid added, and the solution mixed with 100 c.c. of xylene. On shaking the flask vigorously a considerable amount of red colouring matter passed into solution in the xylene, imparting to it a characteristic yellow fluorescence. The flask was then heated on the water-bath for twelve hours, being constantly shaken during the period of heating. The colour of the xylene gradually increased in intensity, and at the end of the time named had become deep red with strong yellow fluorescence; at the same time the colour of the dye solution became weaker, and at the end of the twelve hours had practically disappeared. The xylene solution was then separated and concentrated by distillation, the residue being poured into an evaporating dish and freed as far as possible from xylene by heating on the water-bath. The residue, which solidified on cooling, was washed with a little ether to free it from the last traces of xylene, filtered, and crystallised from light petroleum (b. p. 80—100°). In this way the oxazone was obtained in brown glistening laminæ, with faint green metallic reflex, melting at 205°:

0·2009 gave 15·2 c.c. of nitrogen at 24° and 765 mm. N = 8·63.
$C_{20}H_{18}O_2N_2$ requires N = 8·8 per cent.

The properties of the oxazone correspond in every way with those of 3-diethylaminophenonaphthoxazone, described by Möhlau and Uhlmann.

The hydrochloride, $C_{20}H_{18}O_2N_2,HCl$, was prepared by boiling the oxazone with dilute hydrochloric acid and allowing the deep blue solution to cool, the dark blue crystalline precipitate which then separated being isolated by filtration and dried in an evacuated desiccator. It was analysed by boiling a weighed quantity with water until the filtrate was colourless, filtering, and estimating the amount of hydrochloric acid in the filtrate:

0·2103 gave 0·0858 AgCl. Cl = 10·13.

$C_{20}H_{18}O_2N_2,HCl$ requires Cl = 10·1.

Nile-blue 2B.—The solid commercial dyestuff when warmed with ether or xylene imparted no colour to the solvent, neither did a solution of it when shaken with these liquids give any indication of the presence of the oxazone. A quantity was purified by crystallisation from water and analysed:

0·2210 gave 17·9 c.c. of nitrogen at 18° and 771 mm. N = 9·62.

$C_{27}H_{25}ON_3,HCl$ requires N = 9·5 per cent.

Six grams of the purified colouring matter were dissolved in 1000 c.c. of water, and after being mixed with 10 c.c. of concentrated hydrochloric acid and 200 c.c. of xylene heated on the water-bath, with constant shaking, for twenty-four hours. During the course of heating the upper layer of xylene gradually became intensely fluorescent, but at the end of the time named the dye solution still remained strongly coloured. The xylene solution was therefore removed by aid of the separating funnel and the blue solution of the dye mixed with 100 c.c. of fresh xylene, and the heating continued. Meanwhile the xylene solution from the first extraction was concentrated by distillation, and the residue, after being freed from xylene on the water-bath, washed with ether and crystallised from light petroleum (b. p. 80—100°).

The oxazone prepared in this way was in every way identical with the compound derived from Nile-blue A:

0·2517 gave 18·3 c.c. of nitrogen at 16° and 768 mm. N = 8·64.

$C_{20}H_{18}O_2N_2$ requires N = 8·8 per cent.

The quantity obtained from this experiment was about 0·5 gram. The dye solution which had been mixed with a further quantity of xylene was heated for twenty-four hours longer, when a further amount of about 0·5 gram of the oxazone was obtained on evaporating the xylene solution. Fresh xylene was then again added and the heating continued, the process being repeated until the solution of the dye had become colourless, an operation which required 96 hours in all.

The aqueous solution from these experiments was evaporated on the water-bath to a small bulk, filtered, and the filtrate rendered alkaline by means of dilute caustic soda solution. The oil which then separated was extracted by means of ether, the ethereal solution dried, and freed from ether by evaporation. The small quantity of residual oil boiled at 185° and the following analysis showed it to be benzylamine:

0·2103 gave 0·6037 CO_2 and 0·1607 H_2O. C = 78·32; H = 8·49.

C_7H_9N requires C = 78·5; H = 8·4 per cent.

Formation of 3-Dimethylaminophenonaphthoxazone from New Methylene-blue GG and from New-blue B.

Methylene-blue GG.—The specimen of this colouring matter was obtained from Dr. Grübler, of Leipzig, and had been specially purified for pathological work. It was shown to be pure by the following analysis:

0·2010 gave 20·6 c.c. of nitrogen at 18° and 769 mm. N = 12·12.
$C_{20}H_{19}ON_3$,HCl requires N = 11·9 per cent.

In the first instance the pure dyestuff was extracted with xylene in order to ascertain whether any of the oxazone was present. Since the xylene did not become coloured even on warming it was apparent that the solid dye did not contain any; 3 grams were therefore dissolved in 500 c.c. of water, 5 c.c. of concentrated hydrochloric acid added, and the mixture covered with 100 c.c. of xylene. The xylene solution became strongly coloured on vigorously shaking the flask, showing that the oxazone had commenced to be formed as soon as the colouring matter had dissolved in water. The mixture was heated on the water-bath for fifteen hours, the flask being constantly shaken throughout the time of heating. The xylene solution became gradually deeper in colour as the reaction progressed, and the colour of the dye solution became gradually weaker, until at the end of the fifteen hours the xylene had become deep red in colour with strong yellow fluorescence and the colour of the dye solution had practically disappeared. The layer of xylene was separated and freed from xylene first by distillation and finally by evaporation in an open basin on the water-bath. The solid product when crystallised from xylene was obtained in long, dark coloured needles, appearing brown by transmitted light, which melted at 244° to a red liquid with green metallic reflex:

0·2071 gave 17·0 c.c. of nitrogen at 15·5° and 777 mm. N = 9·85.
$C_{18}H_{14}O_2N_2$ requires N = 9·7 per cent.

The oxazone, which is in all respects identical with the compound prepared by Möhlau and Uhlmann, dissolves in hot dilute hydrochloric acid, forming a deep blue solution from which the *hydrochloride* separates on cooling in dark blue needles with metallic reflex. The salt, which is dissociated by water, was analysed by boiling a weighed quantity with water, filtering, and estimating the amount of hydrogen chloride in the filtrate:

0·2171 gave 0·0948 AgCl. Cl = 10·81.
$C_{18}H_{14}O_2N_2$,HCl requires Cl = 10·9 per cent.

New-blue B.—This colouring matter, which for the purposes of this research was obtained from Messrs. Cassella & Co. of Frankfort-am-

Main, has recently formed the subject of a communication by J. Formánek in a paper dealing with the spectroscopic investigation of the colouring matters of the oxazine series (*Zeitsch. Farb. Ind.*, 1907, 6, 1). The dyestuff is prepared by the action of *asym*-dimethyl-*p*-phenylenediamine on Meldola's blue, and Formánek finds, as a result of the study of the absorption spectra given by a dilute solution, that it is always admixed with a quantity of unchanged Meldola's blue. It was noticed that the dyestuff after repeated recrystallisation did not appear to be a homogeneous substance and that the percentage of nitrogen in the recrystallised product always gave a value too low for a compound corresponding with the constitution assigned to New-blue B. It was therefore not found possible to prepare a pure specimen of the colouring matter, and since Meldola's blue also gives 3-dimethylaminophenonaphthoxazone on boiling with dilute acids, it was difficult to prove conclusively that the oxazone had been formed by the elimination of the dimethyl-*p*-phenylenediamine residue from New-blue B.

The point was, however, settled by the actual isolation of *asym*-dimethyl-*p*-phenylenediamine from the mother liquors after the conversion of the colouring matter into the oxazone.

The process adopted was similar to that used in the previous cases. Six grams of the blue were dissolved in 1000 c.c. of water and, after being mixed with 10 c.c. of concentrated hydrochloric acid and 200 c.c. of xylene, heated on the water-bath, with constant shaking, for twelve hours. After this time the strongly coloured xylene solution was separated and the dye solution again mixed with xylene and heated for a further twelve hours. The xylene solution was then once more separated and the aqueous solution mixed with fresh xylene and again heated for twelve hours. After this process had been repeated five times, the colour of the dye solution had almost disappeared. It was then evaporated to a small bulk on the water-bath, the free hydrochloric acid being in the first instance eliminated by the addition of sodium acetate. The small quantity of unchanged colouring matter in the evaporated solution was then precipitated by means of a solution of tannic acid in sodium acetate, and the clear filtrate rendered alkaline with a dilute solution of caustic soda. The alkaline solution was then extracted with ether, the ethereal extract dried, and evaporated free from ether, when a solid residue was obtained which on crystallisation from a mixture of benzene and light petroleum yielded *asym*-dimethyl-*p*-phenylenediamine in needles melting at 41°:

0·2191 gave 0·5647 CO_2 and 0·1755 H_2O. C = 70·30; H = 8·91.

$C_8H_{12}N_2$ requires C = 70·6; H = 8·8 per cent.

The xylene solutions collected from the above experiments were concentrated by distillation, the residue poured into an evaporating basin, and freed from xylene on the water-bath. The solid residue, on crystallisation from xylene, yielded dark coloured needles melting at 244°, identical with 3-dimethylaminophenonaphthoxazone obtained in the former experiment :

0·2115 gave 17·35 c.c. of nitrogen at 15° and 775 mm. N = 9·87.

$C_{10}H_{14}O_2N_2$ requires N = 9·7 per cent.

Formation of 3-Dimethylaminophenonaphthoxazone from Meldola's Blue.

The specimen of Meldola's blue used in this experiment had been specially purified for pathological work by Dr. Grübler, of Leipzig; the following analysis showed it to be pure :

0·2313 gave 18·00 c.c. of nitrogen at 19° and 770 mm. N = 9·17.

$C_{18}H_{14}ON_2,HCl$ requires N = 9·0 per cent.

In order that Meldola's blue may be completely converted into the oxazone it is necessary (as explained on page 329) that oxidation should take place at the same time, or, in other words, that only half of the blue can be converted into the oxazone at the expense of the other half, which becomes thereby reduced to the leuco-base. The process adopted was as follows.

Three grams of pure Meldola's blue were dissolved in 500 c.c. of water, acidified by the addition of 5 c.c. of concentrated hydrochloric acid, and mixed with 100 c.c. of xylene. On shaking the mixture, the xylene remained colourless, showing that no immediate formation of the oxazone takes place on solution in water. On standing, however, and again shaking, the xylene showed traces of fluorescence, indicating that the process takes place slowly at the ordinary temperature. The mixture was heated on the water-bath for twenty-four hours, after which time the xylene solution had become deeply coloured and strongly fluorescent. These facts are in accordance with the behaviour of Meldola's blue when used as a stain. When the solution of the colour is first prepared it does not possess the power of staining fat red in a pathological section, but after boiling for a short time with dilute acids it possesses this property to a marked degree. The xylene solution was separated, and the dye solution, which contained a considerable quantity of brownish insoluble matter, filtered. All attempts made with the object of purifying this precipitate were unsuccessful, since it rapidly oxidised in the air. It was, therefore, again transferred to the dye solution and the whole placed in a large Winchester-quart bottle, which it half filled, and the bottle shaken on the shaking machine for twelve hours. After this time it was noticed that the precipitate had again passed into solution, and the mixture was therefore transferred to the original flask, covered with 100 c.c. of xylene, and heated with constant shaking for eight hours, The xylene was then again separated and the dye solution subjected to a further shaking for twelve hours, and once again heated with 100 c.c. of xylene for six hours. The xylene solutions from these experiments were concentrated by distillation, the concentrated solution evaporated free from xylene on the water-bath, and the residue crystallised from xylene. 3-Dimethylaminophenonaphthoxazone obtained in this way melted at 244°, and was in all respects identical with the compound prepared in the previous cases:

0·2358 gave 19·35 c.c. of nitrogen at 15·5° and 774 mm. N = 9·83.

$C_{18}H_{14}O_2N_2$ requires N = 9·7 per cent.

It is, of course, impossible by this means to convert the whole of the Meldola's blue into the oxazone, but from the experiments described an amount of 3-dimethylaminophenonaphthoxazone was obtained corresponding with 80 per cent. of the amount of blue taken.

Experiments with Capri-blue GN and Capri-blue GON.

These colouring matters were experimented on in order to ascertain whether derivatives of phenoxazine containing amino- or substituted amino-groups in the *p*-position to the oxazine nitrogen would behave in the same way as the corresponding derivatives of phenonaphthoxazine. Experiments with the two Capri-blues mentioned above, the formulæ of which are given on page 325, showed that these colouring matters did not possess the property of staining fat either when dissolved in water or after boiling for a considerable time with dilute acids. The experiments with xylene bore out these indications, and although after heating an acidified solution of these colouring matters for several days with xylene the xylene solutions became faintly red, yet the amount of substance obtained on evaporating the xylene was too small for further investigation.

My thanks are due to Mr. A. R. Smith, of the Manchester University, for valuable help given during the course of this investigation.

MANCHESTER UNIVERSITY.

XXXVII.—*The Alkaloids of Ergot.*

By GEORGE BARGER and FRANCIS HOWARD CARR.

THE great medicinal importance of ergot has led to numerous chemical researches, which have mostly, however, resulted in little that is definite, possibly owing to the fungoid nature of the plant. As in the case of many drugs, the therapeutic properties of ergot have been attributed to the presence of one or more alkaloids, but several investigators have of late years denied to the ergot alkaloids any part in the specific activity of the drug. The problem is further complicated by the extremely small alkaloidal content (about 0·1 per cent.); this makes the preparation of even a moderate supply of material very expensive.

The first to establish the presence of fixed alkaloids in ergot was Wenzell (*Amer. J. Pharm.*, 1864, **36**, 193), who in 1864 applied the names ecboline and ergotine to two impure resinous preparations giving alkaloidal reactions. His observations were confirmed by Ganser (*Arch. Pharm.*, 1870, **194**, 195). To Tanret, however, belongs the credit of having first obtained from ergot a well-defined crystalline alkaloid, which he named ergotinine in order to distinguish it from the resinous ergotine of Wenzell and others (*Compt. rend.*, 1875, **81**, 896; 1878, **86**, 888; *Ann. Chim. Phys.*, 1879, [v], **17**, 493). From the mother liquors of this base Tanret obtained a further yield of alkaloid in an amorphous form. Since this amorphous alkaloid in other respects closely resembled the crystalline, he called it amorphous ergotinine. Tanret's crystalline alkaloid has been found by all subsequent observers. According to Blumberg (*Inaug. Diss. Dorpat*, 1878) it is probably identical with the picrosclerotine of Dragendorff and Podwyssozki (*Arch. expt. Path. Pharm.*, 1876, **6**, 153); the term sclerocrystalline used by Podwyssozki (*Pharm. Zeitschr. für Russland*, 1883, **22**, 396) is also merely another name for Tanret's alkaloid, and the same applies to the secaline of Jacobj (*Arch. expt. Path. Pharm.*, 1897, **39**, 104). According to Kobert (*Arch. expt. Path. Pharm.*, 1884, **18**, 316) crystalline ergotinine has but slight if any physiological activity, so that when he obtained an impure alkaloidal resin of great toxicity he proposed for it the new name cornutine. According to Tanret (*J. Pharm. Chim.*, 1885, [v], **11**, 309; 1894, [v], **30**, 229), Keller (*Schweiz. Wochenschr. Chem. Pharm.*, 1894, **32**, 121; 1896, **34**, 65), and Meulenhoff (*Ber. Nederl. Maatsch. Pharm.*, 1899, [viii], No. 1; *Ned. Tÿdschr. Pharm.* 1900, **12**, 225, 257), cornutine does not occur as such in ergot, but is an artificial decomposition product of ergotinine, formed by the acid used in its extraction.

In the course of a prolonged investigation of ergot we obtained the second amorphous alkaloid for the first time in a state of purity by crystallising its salts, and were thus able to distinguish it from ergotinine, which is itself crystalline but only yields amorphous salts. Moreover, the amorphous alkaloid is very soluble in alcohol, the crystalline only slightly so. As the second alkaloid is now also recognisable as a chemical individual, and as it has proved to be a substance of great physiological potency, we suggested for it the name ergotoxine in a preliminary communication to the British Association at York (*Chem. News*, 1906, **94**, 89. See also Report of Brit. Med. Assoc. Meeting, Aug. 1906, in *Brit. Med. J.*, Dec. 22nd, 1906, p. 1792). We found in ergotinine considerably more nitrogen than Tanret, and hence were unable to confirm his formula, $C_{35}H_{40}O_6N_4$. As we could not prepare any crystalline ergotinine salts we relied on determinations of the molecular weight of the free alkaloid by physical methods, which made us suggest the provisional formula, $C_{28}H_{32}O_4N_4$. Our analysis of crystalline ergotoxine salts indicated a close relationship between the two alkaloids, and later we proved this relationship by converting ergotoxine into ergotinine by boiling with acetic anhydride; we also obtained a crystalline phosphate closely resembling ergotoxine phosphate by boiling ergotinine with dilute alcoholic phosphoric acid. Soon after our preliminary note was published, there appeared an important paper by Kraft (*Arch. Pharm.*, 1906, **244**, 336), who was, in the first place, concerned with the examination of an ethereal extract of ergot. He lays stress on the following circumstances, which make the separation of the extract into its various constituents very troublesome: the presence of ergosterol and of fat, the feebly acidic nature of the acids, and the feebly basic nature of the alkaloids, the presence of phenolic hydroxyls in the latter giving them also acid properties. Although chemically rather inert, these colloidal bodies "unite among themselves and with fat to form quite stable adsorption compounds." It is, therefore, well nigh impossible to effect a quantitative separation of the alkaloidal from the acid constituents, for instance, by extraction with dilute acetic acid and with ammonia. Kraft concludes that the mere use of solvents and of fractional precipitation is worthless, and that for this reason the numerous ergot substances of Jacobj are but mixtures.

At these conclusions we had ourselves arrived. Acid substances, such as sphacelotoxin, owe their physiological activity to contamination with a powerfully active alkaloid, and we agree with Kraft in emphasising the physiological importance of the alkaloidal as opposed to the acidic constituents of ergot. Without knowledge of our work, Kraft prepared the amorphous alkaloid by fractional precipitation of the sulphate and observed its conversion into ergotinine, his method being to boil a solution of the amorphous alkaloid in methyl alcohol. He regarded this change as due to the elimination of water, and accordingly suggested for the second alkaloid the name hydroergotinine. He did not, however, crystallise any of its salts, nor did he analyse either base. In a recent communication with H. H. Dale (*Arch. Pharm.*, 1906, **244**, 550), one of us expressed doubt as to the validity of Kraft's conception of the amorphous alkaloid as a hydrated ergotinine, because the results of our analyses, taken in conjunction with molecular weight determinations by physical means, appeared to contradict such a view, and led us to interpret the production of ergotinine from ergotoxine by means of acetic anhydride as an acetylation.

Further work, and especially molecular weight determinations of ergotoxine by chemical means, which appear in this case to be more suitable than physical methods, have made us adopt the formula $C_{35}H_{41}O_6N_5$ for ergotoxine. This formula is in satisfactory agreement with our analyses of several of its salts. We now suggest for ergotinine the formula $C_{35}H_{39}O_5N_5$, which requires practically the same percentage composition as $C_{28}H_{32}O_4N_4$ previously suggested, and which (except for the nitrogen) is similar to Tanret's original formula, $C_{35}H_{40}O_6N_4$.

The action of acetic anhydride consists therefore in the removal of a molecule of water, and not as was previously surmised (Barger and Dale, *loc. cit.*) in the introduction of an acetyl group. This earlier surmise is moreover disproved by the fact that no acetic acid is given off on boiling ergotinine with mineral acids.

Kraft showed that the change from the amorphous to the crystalline base is also produced by boiling methyl alcohol, an observation which we have since confirmed. On the basis of this experiment and the production of an amorphous base from ergotinine on standing with dilute acetic acid, Kraft suggested that "the amorphous alkaloid is the hydrate of the crystalline." This theory, which is supported by our own experiments on the action of acetic anhydride and of phosphoric acid, we now regard as definitely established by our analyses.

When the manuscript of this paper was almost complete, our attention was drawn to a recent communication by Tanret (*J. Pharm. Chim.*, 1906, (vi), **24**, 397) in criticism of our preliminary note. By means of a determination according to Dumas, Tanret has confirmed our value for the percentage of nitrogen in ergotinine. He brings evidence to show that our molecular weight determinations by the cryoscopic method in phenol are invalid on account of the production of a phenoxide, which he infers from measurements of the specific rotation. Tanret now suggests for ergotinine the formula $C_{35}H_{40}O_5N_5$, and, as pointed out above, we have ourselves come to reject our original molecular weight determinations and to suggest the formula $C_{35}H_{39}O_5N_5$. Tanret's formula is impossible, since the total number of valencies in the molecule must be an even number. There must be either 39 or 41 hydrogen atoms. We have selected the former number as agreeing much the best with our analyses.

With regard to the relation between ergotoxine and ergot alkaloids other than crystalline ergotinine, there is little doubt that it is largely present in Tanret's so-called amorphous ergotinine, but as this is merely the residue left on evaporating the mother liquor from the crystalline ergotinine, it must contain a proportion of crystallisable alkaloid. This proportion is by no means negligible. As Tanret observed in one of his earlier papers (1879, p. 506), the presence of amorphous ergotinine greatly increases the solubility of the crystalline alkaloid, and in the same paper (p. 507) he attributes the variation in the specific rotation of "amorphous ergotinine" to varying amounts of crystallised ergotinine contained in it. Tanret therefore did not prepare the amorphous alkaloid in the pure state. The amorphous alkaloid is either the same chemical individual as the crystalline or it is not. In the former case it should be possible to crystallise it, and it should have the same specific rotation as the crystalline alkaloid. In the latter case it is confusing to apply the same name to different substances, and a new name must be found. That the amorphous alkaloid is a distinct, although closely related substance, we consider completely established. Tanret deduces the identity of the two alkaloids from the similarity of "their behaviour to precipitating reagents, of their fluorescence, of the mode of formation and properties of their salts, and the amount of acid with which they combine, and finally from the similarity of the characteristic colour reaction which they give with sulphuric acid." But all these points of similarity might be expected in the case of two alkaloids of high molecular weight, differing only by one molecule of water and readily passing into one another. Moreover, there are differences in the characteristics referred to by Tanret. We have found ergotoxine solutions to be distinctly more sensitive to many alkaloidal precipitants than ergotinine solutions of the same strength. As for the salts, few if any ergotinine salts have been obtained crystalline, whereas we have been able to crystallise quite a number of ergotoxine salts. Kraft (*loc. cit.*) has shown that a remarkable difference exists between the solubilities of the two sulphates, that of the amorphous alkaloid requiring 8,000 parts, and that of the crystalline only 500 parts of water for solution. We have confirmed Kraft's observations on this point. Tanret himself has pointed out the difference between the solubilities of the two alkaloids in alcohol and the difference in their specific rotations. Kraft and we ourselves have transformed one alkaloid into the other by chemical means, and finally, our analyses show that the two alkaloids have a different percentage composition. The term amorphous ergotinine must therefore be restricted to such specimens of the crystallisable alkaloid as can, for instance, be prepared by precipitating a solution in dilute acetic acid by ammonia.

The question of the relation between ergotoxine and cornutine is somewhat more difficult. Kobert's method of preparation makes it probable that his substance contains ergotoxine. On the other hand, certain of the most striking symptoms described by Kobert as characteristic of the toxic effects of cornutine are not produced by ergotoxine. This made it impossible to adopt for our alkaloid the name cornutine which Kobert has associated, not with chemical properties, but with the production of a certain physiological picture (see also Barger and Dale, *Arch. Pharm.*, 1906, **244**, 554).

On the other hand, the hydroergotinine recently described by Kraft is undoubtedly identical with ergotoxine, previously described by ourselves. After an examination of ergotoxine salts prepared by us, Dr. Kraft has recently informed us that he shares our view as to the identity of the alkaloids. He, too, has now succeeded in crystallising ergotoxine (hydroergotinine) sulphate.

According to experiments of H. H. Dale, ergotoxine produces in doses of a few milligrams not only the characteristic reactions of ergot described by him (*J. Physiol.*, 1906, **34**, 163), but also gangrene of the cock's comb and other ergot effects described by Kobert and others to sphacelenic acid. Crystalline ergotinine, uncontaminated with ergotoxine, either does not give these effects at all, or only to a slight extent, the difference being possibly due to the difficulty of keeping ergotinine in solution in the body fluids.

Ergotinine.

This alkaloid was prepared by various methods, in the first place according to that given by Tanret, starting from an alcoholic extract of the drug. Great difficulty was experienced in extracting with ether, and in washing the ether with water, as the alkali present led to the formation of a resin soap, which made the separation into an ethereal and an aqueous layer very tedious. Meulenhoff mentions the same difficulty. For the preparation of ergotinine on a small scale, it is best to take advantage of the fact that it can be extracted by ether; this is the basis of Keller's method. He first extracted the ergot with light petroleum to remove the oil and then with ether to remove the alkaloid. We agree with Kraft that there is no advantage in the preliminary extraction with light petroleum.

If the ethereal extract is freed from ether and the resulting oil mixed with light petroleum, most of the alkaloid, together with a yellow colouring matter and other substances, is precipitated (Jacobj's chrysotoxin), but a small part of the alkaloid remains in the oil and can be extracted with dilute acids. The alkaloid obtained in this manner is uncontaminated with resin and at once yields white crystals from alcohol.

The salts of the ergot alkaloids with inorganic acids are very slightly soluble in water. Hence Tanret extracted the ethereal solution with citric acid, and Kraft used tartaric acid. When working on a large scale, however, the slight solubility of the chloride and especially of the bromide may be put to account. The residue left on evaporation of the alcoholic tincture is extracted with light petroleum to remove fat and oily matter; it is then dissolved in ethyl acetate and shaken with citric acid solution. Sodium bromide or hydrobromic acid is added and the precipitated hydrobromides of the alkaloids are collected. A rough separation of ergotinine from ergotoxine can be effected by repeated shaking of the solution of the mixed hydrobromides in dilute caustic soda with ether; in this way the ergotinine is removed first. Finally, the ergotinine is crystallised from alcohol, leaving ergotoxine and impurities in the mother liquor.

Composition of Ergotinine.

For analysis the alkaloid was recrystallised from absolute ethyl alcohol and was dried in a vacuum over sulphuric acid or in the steam oven. It is not hygroscopic.

I. 0·1511 gave 0·3793 CO_2 and 0·0851 H_2O. C = 68·47; H = 6·30.
II. 0·1174 ,, 0·2966 ,, ,, 0·0700 ,, C = 68·90; H = 6·66.
III. 0·1598 ,, 0·4031 ,, ,, 0·0912 ,, C = 68·80; H = 6·38.
IV. 0·1557 ,, 0·3914 ,, ,, 0·0881 ,, C = 68·55; H = 6·33.
V. 0·1947 ,, 0·4889 ,, ,, 0·1160 ,, C = 68·48; H = 6·66.
VI. 0·1537 ,, 0·3871 ,, ,, 0·0904 ,, C = 68·68; H = 6·58.
VII. 0·1453 ,, 0·3674 ,, ,, 0·0871 ,, C = 68·96; H = 6·70.

In the last combustion the substance was mixed with cupric oxide.

Mean C = 68·69; H = 6·52.

$C_{35}H_{39}O_5N_5$ requires C = 68·91; H = 6·45 per cent. Tanret's analysis gave C = 68·57; H = 6·79 per cent.

I. 0·1320 gave 13·1 c.c. N at 17° and 770 mm. N = 11·7.
II. 0·1331 ,, 13·0 ,, ,, ,, 17 ,, 770 ,, N = 11·5.
III. 0·2156 ,, 22·0 ,, ,, ,, 21 ,, 767 ,, N = 11·7.
IV. 0·2283 ,, 22·0 ,, ,, ,, 12·5 ,, 774 ,, N = 11·6.

$C_{35}H_{39}O_5N_5$ requires N = 11·5 per cent.

Tanret found in 1879 by Will and Varrentrapp's method 8·71 and

9·26 per cent. of nitrogen, and quite recently by Dumas' method 11·76 per cent., so that the former method is once more shown to be unsatisfactory.*

Molecular Weight Determinations.

I. By the cryoscopic method in acetic acid:

0·210 in 12·85 acetic acid gave $\Delta t = -0·100°$; M.W. = 634.
$C_{35}H_{39}O_5N_5$ requires M.W. = 609.

The suitability of acetic acid as a solvent for an alkaloid we infer from an experiment with strychnine, which gave a good value (342, calc. 334) for the molecular weight.

II. By the analysis of the platinichloride, prepared by dissolving ergotinine in acetone, adding hydrochloric acid and an aqueous solution of platinic chloride, evaporating the acetone in a vacuum desiccator, filtering off the precipitated salt from the residual water and washing with water.

0·1740 of the salt left on ignition 0·220 Pt; Pt = 11·6.
$(C_{35}H_{39}O_5N_5)_2,H_2PtCl_6$ requires Pt = 11·9 per cent.
$(C_{35}H_{41}O_6N_5)_2,H_2PtCl_6$,, Pt = 11·6 ,,

The second formula is applicable if the ergotinine is changed to ergotoxine by the acid present.

The formula $C_{35}H_{39}O_5N_5$ agrees with Tanret's old analyses of the amorphous hydrochloride and hydrobromide of ergotinine, and with his recent analyses of the likewise amorphous platinichloride (found: Pt = 11·66, 11·83; Cl = 12·69; calculated Pt = 11·95; Cl = 13·06). We were first led to adopt this formula by analyses of crystalline ergotoxine salts, which gave us the corresponding formula $C_{35}H_{41}O_6N_5$ for ergotoxine. Before this time we preferred the formula $C_{28}H_{32}O_4N_4 = 488$, based on the following molecular weight determinations in which the ergotinine apparently underwent decomposition.

I. By the cryoscopic method in phenol:

0·1775 in 14·57 phenol gave $\Delta t = 0·32°$; M.W. = 516.
0·3715 ,, ,, ,, ,, $\Delta t = 0·535°$; M.W. = 477.

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* At first we thought that the discrepancy with Tanret's original figures might be due to the presence of methane in our nitrogen (compare Dunstan and Carr, Proc., 1896, **12**, 48; and Haas, Trans., 1906, **89**, 570). We therefore availed ourselves of the kindness of Dr. P. Haas, who has recently investigated this source of error (*loc. cit.*). He performed the first two of the determinations quoted, mixing the substance with cuprous chloride and proving the absence of methane in the nitrogen by explosion with oxygen. For his help in this matter we tender him our best thanks. In subsequent determinations of the nitrogen in ergotinine and in ergotoxine salts we always mixed the substance with cuprous chloride. Without this precaution, too much nitrogen was found; for example, 12·0 per cent. in ergotinine.

II. By a microscopic method, due to one of us (Trans., 1905, **87**, 1756), 0·0858 in 1·06 pyridine at 80° = 0·17 – 0·18 mole.; M.W. = 463.

The number of carbon, oxygen, and nitrogen atoms in ergotinine seems now to be established with tolerable certainty. The number of hydrogen atoms is less certain; it must, however, be an odd number, in order to make the total number of valencies even, and can therefore not be forty, as Tanret suggests. From our analyses we conclude that there are very probably 39, possibly 41 hydrogen atoms in ergotinine. The formula $C_{35}H_{39}O_5N_5$ requires 6·45 per cent., the formula $C_{35}H_{41}O_5N_5$ 6·76 per cent., of hydrogen: on the average we found 6·52 per cent. in good agreement with the first formula, since the amount of water found in combustions is generally somewhat too high.

Properties of Ergotinine.

Ergotinine crystals consist of long needles, the sides of which are not quite parallel; the ends are symmetrically replaced by a pair of faces, and the extinction is straight.*

When placed in a bath at 210° and heated further ergotinine sinters, darkens and melts at temperatures up to 229° (corr.). Kraft gives m. p. 219°, Tanret 205°. We have also frequently found 219—220° (uncorr.). The decomposition point is not very characteristic and depends greatly on the rate of heating.

Solubility determinations were made by shaking the powdered alkaloid in the cold with the solvent, and by rapidly filtering the boiling solution. One part of ergotinine dissolves at 10° in 312 parts by weight of absolute ethyl alcohol, at 18° in 292 parts of alcohol, in 1,020 parts of absolute ether, in 91 parts of ethyl acetate, and in 26 parts of acetone; further, in 77 parts of boiling benzene, 52 parts of boiling ethyl alcohol, and 56 parts of boiling methyl alcohol. It is extremely soluble in cold chloroform, moderately so in amyl alcohol, methylal or xylene, and insoluble in light petroleum.

The determination of the specific rotation at 10° in a saturated solution in ethyl alcohol, prepared by shaking in the cold, gave $\alpha_D + 1{\cdot}91°$; $l = 0{\cdot}22$ dcm.; $c = 0{\cdot}257$; $[\alpha]_D + 338°$.

Tanret found + 334° and + 336°. Five different specimens of ergotinine, in alcoholic solutions prepared by boiling, with $c = 0{\cdot}172$—$0{\cdot}257$, gave at 10—18° $[\alpha]_D$ + 320°, + 328°, + 326°, + 330°, + 327°; mean + 328°.

The rotatory power of an alcoholic solution of ergotinine falls through prolonged boiling. The solution saturated in the cold, and referred to above, was boiled under a reflux condenser. $[\alpha]_D$, originally +338°, fell after five minutes to +327°, after one hour to +300°, after three hours' boiling to +242°. In another experiment a specimen of ergotinine, prepared from ergotoxine by acetic anhydride, had $[\alpha]_D$ +388°, but after it had been boiled for half an hour the same solution gave $[\alpha]_D$ +326°. The fall of rotatory power is accompanied by a disappearance of crystallisable alkaloid. We have frequently noticed a certain deficit when recrystallising a given quantity of pure ergotinine, however carefully the successive mother liquors were concentrated.

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* For this description of ergotinine crystals and for others of the crystals of ergotoxine salts given later, we are indebted to Prof. W. J. Pope and tender him our best thanks for his assistance in this respect.

The destructive action of hot alcohol is also shown by an experiment in which 0·1 gram of ergotinine was heated with 3 c.c. of alcohol in a sealed tube at 100° for twelve hours. More than half was destroyed. Tanret, in his recent publication, has also pointed out that a solution of the crystalline alkaloid always leaves a partially amorphous residue on evaporation. We further determined the specific rotation in other solvents and found higher values than in alcohol.

In acetone: α_D $+0{\cdot}86°$; $l=1$ dcm.; $c=0{\cdot}234$; $[\alpha]_D$ $+367°$.
In ethyl acetate: α_D $+0{\cdot}64°$; $l=1$ dcm.; $c=0{\cdot}176$; $[\alpha]_D$ $+363°$.
In chloroform: α_D $+2{\cdot}03°$; $l=1$ dcm.; $c=0{\cdot}514$; $[\alpha]_D$ $+396°$.

The lowering of the specific rotation of ergotinine, produced, as Tanret showed, by the addition of acids and alkalis to the solution, seems to depend in the first place on a transformation to ergotoxine and possibly also on racemisation. For instance, the addition of one molecular equivalent of phosphoric acid to an alcoholic ergotinine solution lowered $[\alpha]_D$ from +328° to +319°, and after boiling for fifteen minutes to +195°. After boiling with fifteen molecular proportions of phosphoric acid the value was +41°. Under similar conditions sulphuric acid produced a much more rapid lowering of the rotatory power, which presumably depends on the concentration of hydrogen ions.

So far we have not been able to prepare any undoubted ergotinine salts in the crystalline state. Even when crystals are obtained, there is the possibility of the formation of the corresponding ergotoxine salt as a result of hydrolytic action of the acid used. In an attempt to crystallise ergotinine phosphate we added the calculated quantity of phosphoric acid to an alcoholic solution of the base, and concentrated the solution in a vacuum desiccator. The salt which separated out was gelatinous and was filtered off; on decomposition with ammonia it readily yielded the characteristic prisms of ergotinine. The filtrate from the amorphous salt was concentrated further, and finally yielded a small quantity of sphærites and diamond-shaped plates. These were decomposed with ammonia in the same way as the amorphous salt, but yielded an amorphous base, which withstood all attempts at crystallisation and was very readily soluble in alcohol. Later, it was found that a good yield of the same crystals could be produced by boiling the solution for a short time, and that they probably represent ergotoxine phosphate.

It is therefore probable that the crystalline sulphate mentioned by Tanret, and possibly also the halides which he analysed, together with the crystalline chloride obtained by Keller, were salts of ergotoxine. As we have shown, ergotinine is readily decomposed by very dilute phosphoric acid in boiling alcoholic solution, and, apparently, transformed to ergotoxine phosphate; Kraft has found that ergotoxine is even produced in dilute acetic acid solution in the cold. We have also obtained from ergotinine small quantities of a crystalline picrate, but are unable to say whether it is a salt of ergotinine or ergotoxine.

Keller found that the amorphous hydrochloride formed by precipitating an ethereal solution of the base with hydrochloric acid is soluble in water, but gives a precipitate with hydrochloric acid. This he attributed to the formation of an insoluble acid salt. We are unable to share this view. The salt is not only precipitated by hydrochloric acid, but also by sodium chloride, sodium acetate, and sodium tartrate; not, however, by acetic acid, tartaric acid, carbamide, or sucrose. The precipitation therefore depends on the presence of ions and the solution of the salt is a colloidal one. Ergotoxine phosphate also gives a colloidal solution (see later). It is probable that the reason why organic acids are more suitable for the extraction of ergotinine from an ethereal solution than inorganic acids, depends on the small degree of ionisation of organic acids.

The characteristic colour reactions for ergotinine have been described by Tanret (addition of concentrated sulphuric acid to a solution of ergotinine in ether or in ethyl acetate, giving a transitory orange coloration, changing to blue) and by Keller (anhydrous ferric chloride, added to ergotinine in concentrated sulphuric acid, changes the colour from pale yellow, through orange, crimson, and green to a permanent dark blue). Both these reactions are, however, given by ergotoxine with the same intensity as by ergotinine, since the two alkaloids naturally undergo the same decomposition by sulphuric acid. The behaviour of ergotinine solutions towards alkaloidal precipitants will be discussed later and compared with that of ergotoxine solutions. For a reply to Tanret's recent criticism of our view, that ergotinine is physiologically inert, we must for the present refer to the paper by Barger and Dale (*loc. cit.*).

Ergotoxine.

This alkaloid was prepared as follows. The caustic liquor from which the ergotinine had been extracted (see above, under preparation of ergotinine) was neutralised, again rendered alkaline with sodium carbonate, and extracted with ether. The residue left after evaporation of the ether, together with that from the ergotinine mother liquors, was dissolved in 80 per cent. alcohol and a slight excess of phosphoric acid in alcohol added. After standing for a few days the ergotoxine phosphate crystallised out and was recrystallised from alcohol. In the purest form in which we have obtained this alkaloid it formed a light white powder, which when heated began to soften at about 155° and gradually melted at 162—164°. It is more soluble in organic solvents than ergotinine, notably in cold alcohol. In ether it is but slightly soluble. All attempts to crystallise it, for instance, by the slow evaporation of its ethereal solution in a desiccator, have failed.

For analysis, the alkaloid was liberated from the pure oxalate with sodium carbonate and dissolved in ether. After careful washing, the solution was evaporated in a vacuum desiccator and the residual alkaloid dried until of constant weight.

0·2553 gave 0·6224 CO_2 and 0·1503 H_2O. C = 66·49; H = 6·59.
0·1982 „ 0·4808 CO_2 „ 0·1164 H_2O. C = 66·16; H = 6·58.
$C_{35}H_{41}O_6N_5$ requires C = 66·93; H = 6·59 per cent.

For the establishment of this formula we mainly rely, however, on our analysis of the crystalline salts.

For the specific rotation of ergotoxine in alcoholic solution we have obtained the following figures:—

I. Prepared from the oxalate by ammonia and ether,

$$a_D + 0·6°;\ l = 1\text{ dcm.};\ c = 1·624;\ [a]_D + 40·6°.$$

II. By the addition of the theoretical quantity of caustic soda to the phosphate dissolved in alcohol,

$$a_D + 0·31°;\ l = 1\text{ dcm.};\ c = 0·80;\ [a]_D + 44·5°.$$

III. Prepared from the oxalate by sodium carbonate and ether,

$$a_D + 0·61°;\ l = 1\text{ dcm.};\ c = 1·37;\ [a]_D + 45·3°.$$

IV. Prepared from the oxalate by sodium carbonate and ether,

$$a_D + 0·10°;\ l = 1\text{ dcm.};\ c = 0·45\text{ m.};\ [a]_D + 22·2°.$$

V. Prepared from the oxalate by ammonia and ether,

$$a_D + 0·005°;\ l = 1\text{ dcm.};\ c = 0·884;\ [a]_D + 0·6°.$$

All these values are very much lower than those given by Tanret for "amorphous ergotinine," which must have contained a considerable proportion of crystallisable alkaloid. At the same time we are unable to explain the want of constancy in our values unless this is due to a varying degree of racemisation; this point requires further investigation.

We have studied the action of alkaloidal precipitants on ergotoxine and on ergotinine in some detail in order to bring out the points of difference between the two alkaloids. The following table gives approximately the most dilute solutions of each alkaloid in which the various reagents still produced a faint opalescence. The solutions were made by dissolving ergotoxine phosphate and ergotinine in the minimum quantity of glacial acetic acid and diluting with distilled water:

Reagent.	One part of ergotinine in	One part of ergotoxine in
Potassium mercuric iodide	1,000,000	2,000,000
Iodine in potassium iodide	200,000	1,000,000
Picric acid	50,000	50,000
Phosphomolybdic acid	40,000	80,000
Phosphotungstic acid	40,000	40,000
Auric chloride	20,000	20,000
Potassium chromate	20,000	20,000
,, dichromate	10,000	20,000
,, ferrocyanide	10,000	10,000
,, ferricyanide	10,000	10,000
,, sulphocyanate	10,000	20,000
Platinic chloride	10,000	10,000
Bromine water	10,000	20,000
Tannic acid	8,000	20,000
Potassium fluoride	50,000	50,000
,, iodide	20,000	20,000
,, bromide	6,000	15,000
Sodium chloride	4,000	8,000
,, sulphate	500	7,000

It will be seen that an ergotinine solution is distinctly less sensitive to a number of reagents than an ergotoxine solution of the same strength. The best reagent is potassium mercuric iodide, which, according to Tanret, precipitates a solution of 1 part ergotinine in 1,240,000 parts of water. The limits for the last three salts depend largely on the amount of salt added and are somewhat arbitrary.

Ergotoxine Salts.

These salts were mostly prepared by adding a concentrated alcoholic solution of the acid drop by drop to a dilute ethereal solution of the base obtained from the phosphate. The reaction is best carried out in a tall stoppered cylinder, so that after shaking the salt readily settles down and leaves a clear, supernatant solution. As soon as no further precipitate is formed, the salt is washed a few times with dry ether by decantation, collected at the pump, and dried in a vacuum. In the case of mineral acids, it is very important to avoid excess, which brings about decomposition.

A sulphate, nitrate, hydrochloride, hydrobromide, two oxalates, and a tartrate, have been obtained crystalline, but only the phosphate, the oxalates, and the hydrochloride have so far been studied. The salts of ergotoxine with inorganic acids are very sparingly soluble in water, but readily so in hot alcohol, from which they can be crystallised. The salts with organic acids are more soluble in alcohol and are best crystallised by adding ether to their solutions in cold alcohol.

Ergotoxine is, like ergotinine, a very feeble base and does not combine with more than one equivalent of acid. Its salts have an acid reaction; a crystal of the oxalate, for instance, produces a red spot when placed on moist blue litmus paper.

Ergotoxine Phosphate, $C_{35}H_{41}O_6N_5,H_3PO_4,H_2O$.

This is the most easily purified of the ergotoxine salts which we have so far examined, and was the starting-point in the preparation of the other salts. The crude phosphate obtained in the manner described under ergotoxine is decomposed by sodium carbonate, yielding the base, and this is precipitated in ethereal solution with phosphoric acid. After washing, the precipitated salt is dried and crystallised from alcohol, using 50 c.c. of 90 per cent. boiling alcohol for 1 gram of salt. With these proportions crystallisation should begin slowly, after one or two hours. It is important to use alcohol containing a little water, as the phosphate is much less soluble in absolute alcohol. When the crude salt is crystallised it separates in groups of needles radiating from centres and showing straight extinction, and, when pure, in isolated needles melting with decomposition at 186—187° (the bath being heated to 180° before the introduction of the substance).

One part of ergotoxine phosphate dissolves in 313 parts of cold, and in 14 parts of boiling alcohol of 90 per cent.

By shaking ergotoxine phosphate with cold distilled water, a typical colloidal solution can be obtained, containing 1 per cent. of the salt. This solution froths and is strongly opalescent, but does not deposit any of the salt on standing. The addition of an electrolyte (sodium acetate, sodium phosphate) converts the hydrosol into a gel. If equal volumes of *N*-hydrochloric, oxalic, phosphoric, or acetic acids are added to the solution, the degree of precipitation is in the order named, that is, in that of the conductivities of the acids. The hydrochloric acid produces a thick jelly, so that the test tube can be inverted, while the acetic acid leaves the solution fluid. It seems probable that this is one of the reasons why phosphoric and most organic acids are to be preferred to the stronger mineral acids in the extraction of ergot alkaloids. It has been shown already that a colloidal solution of ergotinine hydrochloride is precipitated by electrolytes in a similar manner.

For analysis the phosphate was recrystallised two or three times from alcohol, and dried in a vacuum over sulphuric acid till constant. The salt crystallises with one molecule of water.

0·1696 lost 0·0042 H_2O; $H_2O = 2·42$.

$C_{35}H_{41}O_5N_5,H_3PO_4,H_2O$ requires $H_2O = 2·48$ per cent.

The anhydrous salt is hygroscopic, so that the boat was always enclosed in a weighing tube.

I. 0·1254 gave 0·2650 CO_2 and 0·0713 H_2O. C = 57·63 ; H = 6·37.
II. 0·1654 ,, 0·3491 ,, ,, 0·0925 ,, C = 57·56 ; H = 6·26.
III. 0·1552 ,, 0·3278 ,, ,, 0·0843 ,, C = 57·60 ; H = 6·08.

$C_{35}H_{41}O_6N_5,H_3PO_4$ requires C = 57·89 ; H = 6·11 per cent.

In each of the above three analyses a different specimen was used.

In the following two, the substance was mixed with cupric oxide, leading to somewhat higher figures, especially for the hydrogen.

0·1698 gave 0·3634 CO_2 and 0·1020 H_2O. C = 58·37 ; H = 6·71.
0·0916 ,, 0·1954 ,, ,, 0·0570 ,, C = 58·17 ; H = 6·99.

For the determination of the nitrogen the substance was mixed with cuprous chloride. The phosphoric acid was determined by heating the salt on the water-bath with ammonia, and filtering off the alkaloid.

0·1128 gave 9·4 c.c. N at 19° and 768 mm. N = 9·7.
0·1787 ,, 14·5 c.c. N at 14·5° and 760 mm. N = 10·0.
0·3688 ,, 0·0588 Mg_2,P_2O_7 ; $H_3PO_4 = 14·1$.

$C_{35}H_{41}O_6H_5,H_3PO_4$ requires N = 9·7 ; $H_3PO_4 = 13·5$ per cent.

Ergotoxine Hydrochloride, $C_{35}H_{41}O_6N_5,HCl$.

When prepared by precipitation of an ethereal ergotinine solution this salt forms minute diamond-shaped plates, and very thin and very long square-ended needles, showing straight extinction and melting at 205° (bath previously heated to 190°). For recrystallisation 0·3 gram of the salt was dissolved in 4—5 c.c. of 90 per cent. alcohol, by warming on the water-bath, and, after cooling, ether was added in quantities of a few drops at a time.

The salt is very unstable and therefore difficult to purify.

Determination of chlorine :

1. By precipitating the solution in 90 per cent. alcohol with alcoholic silver nitrate :

0·1055 gave 0·0229 AgCl ; Cl = 5·35.

2. By Carius' method :

0·1478 gave 0·0348 AgCl ; Cl = 5·8.

$C_{35}H_{41}O_6N_5,HCl$, requires Cl = 5·35 per cent.

Normal Ergotoxine Oxalate $(C_{35}H_{41}O_6N_5)_2,H_2C_2O_4$.

By adding a solution of oxalic acid in alcohol to a solution of ergotoxine in ether, so that the base is in excess, the normal oxalate was formed. The precipitate was washed and dried, and crystallised by gradually adding dry ether to a cold concentrated solution of the salt in 80 per cent. alcohol. After each addition of ether the solution was set aside for crystallisation. If absolute alcohol is used, crystals are much more difficult to obtain.

The salt forms elongated, rectangular plates, showing straight extinction and melting at 179° (the bath being previously heated to 170°). It is soluble in five parts of boiling absolute alcohol, and in twelve parts of alcohol at 25°.

0·1579 gave 0·3727 CO_2 and 0·0949 H_2O. C = 64·35; H = 6·72.
0·1168 „ 0·2735 „ „ 0·0652 „ C = 63·83; H = 6·24.
0·1920 „ 14·4 c.c. N at 15·5° and 768 mm. N = 10·70.
0·2040 „ 18·3 c.c. N at 13° and 771 mm. N = 10·76.
$(C_{35}H_{41}O_6N_5)_2,H_2C_2O_4$ requires C = 64·24; H = 6·29; N = 10·42. per cent.

The oxalic acid was determined by adding ammonia, extracting with ether, and precipitating the oxalic acid in the aqueous solution with calcium acetate.

0·203 gave 0·0077 CaO. $H_2C_2O_4$ = 5·7.
$(C_{35}H_{41}O_6N_5)_2,H_2C_2O_4$ requires $H_2C_2O_4$ = 6·6 per cent.

Acid Ergotoxine Oxalate, $C_{35}H_{41}O_6N_5,H_2C_2O_4$.

This salt is formed by shaking a solution of the alkaloid in xylene with excess of a 1 per cent. solution of oxalic acid. On crystallisation from alcohol and acetone it gave minute prisms, melting at 179° with decomposition. It does not crystallise so well as the normal oxalate.

0·2280 gave 0·5137 CO_2 and 0·1313 H_2O. C = 61·45; H = 6·44.
0·1770 „ 0·3988 „ „ 0·1030 „ C = 61·44; H = 6·51.
0·2322 „ 0·5256 „ „ 0·1324 „ C = 61·73; H = 6·38.
0·2108 „ 0·0136 CaO; $H_2C_2O_4$ = 10·5.
$C_{35}H_{41}O_6N_5,H_2C_2O_4$ requires C = 61·88; H = 6·04; $H_2C_2O_4$ = 12·6 per cent.

The Transformation of the Ergot Alkaloids into one another.

The transformation of the amorphous alkaloid into the crystalline was first observed by Kraft by boiling a solution of the former in methyl alcohol under a reflux condenser. On cooling, ergotinine crystallised out. Kraft also observed the formation of hydroergotinine (as he called the amorphous alkaloid), when a solution of ergotinine in 3 per cent. acetic acid is left standing for some days at the laboratory temperature.

Shortly before the publication of Kraft's results, we had independently observed the formation of ergotinine from ergotoxine in an attempt to acetylate the latter alkaloid. With this end in view, 0·64 gram of ergotoxine was boiled with 10 c.c. of acetic anhydride for a few seconds. The solution was then poured into water and stirred vigorously. The solution of the alkaloidal acetates was separated from a small quantity of a dark resin, and the alkaloids were precipitated in the filtrate with ammonia, collected on a filter, and dried in a vacuum. The alkaloidal precipitate weighed 0·49 gram, and required for complete solution about 25 c.c. of boiling absolute alcohol, whereas the ergotoxine employed was soluble in very much less alcohol. On cooling, 0·13 gram of ergotinine separated out, and on concentration of the mother liquor 0·06 gram more, in all therefore about 30 per cent. of the theoretical yield. The identity with natural ergotinine results from the following:

(1) The melting point was 220°, and remained unchanged when the substance was mixed with natural ergotinine.

(2) the composition: 0·1153 gave 0·2895 CO_2 and 0·0668 H_2O. C = 68·48; H = 6·48.

$C_{35}H_{39}O_5N_5$ requires C = 68·91; H = 6·45.

(3) The specific rotation in alcoholic solution:

$$\alpha_D + 0·69°;\ l = 1 \text{ dcm.};\ c = 0·200;\ [\alpha]_D + 345°.$$

In a similar experiment the yield of ergotinine was 25 per cent.; for the specific rotation we found:

$$\alpha_D + 0·95°;\ l = 1 \text{ dcm.};\ c = 0·245;\ [\alpha]_D + 388°.$$

After boiling the alcoholic solution for half an hour:

$$\alpha_D + 0·77°;\ l = 1 \text{ dcm.};\ c = 0·231;\ [\alpha]_D + 326°.$$

The mean value previously found for natural ergotinine after boiling with alcohol was $[\alpha]_D + 328°$.

At first we were unable to repeat Kraft's experiment with methyl alcohol, perhaps because we used ergotoxine prepared by heating the phosphate on the water-bath with ammonia and filtering. Later, at Dr. Kraft's suggestion, we liberated the base with sodium carbonate, extracted with ether, dried the ethereal solution with sodium sulphate, and evaporated it in a vacuum over paraffin wax. We then obtained from 0·139 gram of ergotoxine, dissolved in 2·4 c.c. methyl alcohol after four hours' boiling on the water-bath, 0·031 gram of ergotinine = 23 per cent.

This specimen gave:

$$\alpha_D + 0{\cdot}90^\circ;\ l = 1 \text{ dcm.};\ c = 0{\cdot}1244;\ [\alpha]_D + 328^\circ.$$

In a similar experiment, when ammonia was used to liberate the base, we obtained a somewhat smaller yield, and in no case was the transformation even approximately quantitative. As we have already observed, we infer from our experiments on the optical rotation of ergotinine that the alkaloid undergoes decomposition by prolonged boiling in alcoholic solution. Since we originally regarded ergotinine as acetylergotoxine, we attempted to hydrolyse it by means of an acid, and selected phosphoric acid because the phosphate is the most characteristic of ergotoxine salts. 0·3 gram of ergotinine, which would require nearly 20 c.c. of boiling absolute alcohol for solution, was heated on the water-bath with 6 c.c. of alcohol containing 1¼ molecular proportions of phosphoric acid. At 70° the ergotinine did not readily dissolve, but after boiling for fifteen minutes solution was complete. On standing overnight, 0·2 gram of minute diamond-shaped plates separated out, consisting of long needles of which each end is symmetrically replaced by two dome faces; the extinction is parallel to the long edge of the crystals. They were found to be the phosphate of an amorphous base. On recrystallisation from alcohol and ether much larger plates were obtained, mostly hexagonal or triangular in shape, and differing completely from the slender prisms of ergotoxine phosphate already described. Nevertheless, both phosphates melted at 186—187°, and a mixture of the two showed the same melting point. This new phosphate was converted into the oxalate, which melted at the same temperature as normal ergotoxine oxalate, and resembled it in crystalline form. Finally, the oxalate was reconverted into the phosphate, which was found to have preserved its original crystalline form. Its identity with ergotoxine phosphate we have not as yet definitely established for want of material, but possibly the one is a racemic modification of the other. Both salts show great physiological activity.

In order to prove the absence of acetyl groups in ergotinine, its solution in 20 per cent. aqueous phosphoric acid was distilled with steam. No acid passed over. On neutralisation and concentration the solution yielded the typical prisms of ergotoxine phosphate.

In conclusion, we wish to acknowledge our indebtedness to Mr. W. C. Reynolds, B.Sc., for much help in the isolation of the alkaloids, and to Mr. A. J. Ewins, B.Sc., for valuable assistance throughout the work.

The Wellcome Physiological Research Laboratories,
Herne Hill, London, S.E.

XXXVIII.—*ααγ-Trimethyl- and ααγγ-Tetramethyltricarballylic Acids and αγ-Dimethylbutane-αβδ-tricarboxylic Acid.*

By HERBERT HENSTOCK and CHARLES HENRY GRAHAM SPRANKLING.

IN a paper by Bone and Sprankling (Trans., 1902, **81**, 29) a general method is described for the synthesis of alkyltricarballylic acids, based on the interaction of the sodium compounds of cyanosuccinic esters and bromo-fatty esters in alcoholic solution, by means of which these authors were able to undertake a systematic study of the properties of α-monomethyl-, αα-, and αγ-dimethyltricarballylic acids, their anhydro-acids, and methyl hydrogen salts. We have now extended the investigation to the ααγ-trimethyl- and ααγγ-tetramethyltricarballylic acids and also to αδ-dimethylbutane-αβδ-tricarboxylic acid, the properties of which are described in the present communication.

In conformity with the experiments of Bone and Sprankling, we expected to obtain ααγ-trimethyltricarballylic acid from the hydrolysed product of the interaction of either (*a*) the sodium compound of ethyl β-methylcyanosuccinate and ethyl α-bromo*iso*butyrate, or of (*b*) the sodium compound of ethyl ββ-dimethylcyanosuccinate and ethyl α-bromopropionate, as shown by the following equations:

$$(a)\ \mathrm{CO_2Et{\cdot}CNa(CN){\cdot}CHMe{\cdot}CO_2Et + CMe_2Br{\cdot}CO_2Et =}$$
$$\mathrm{CO_2Et{\cdot}C(CMe_2{\cdot}CO_2Et)(CN){\cdot}CHMe{\cdot}CO_2Et + NaBr.}$$

$$(b)\ \mathrm{CO_2Et{\cdot}CNa(CN){\cdot}CMe_2{\cdot}CO_2Et + CHMeBr{\cdot}CO_2Et =}$$
$$\mathrm{CO_2Et{\cdot}C(CHMe{\cdot}CO_2Et)(CN){\cdot}CMe_2{\cdot}CO_2Et + NaBr.}$$

Whilst ααγγ-tetramethyltricarballylic acid should be similarly obtained from the hydrolysed product of the interaction of the sodium compound of ethyl ββ-dimethylcyanosuccinate and ethyl α-bromo*iso*butyrate.

We found, however, that as long as alcohol was employed as the diluting medium for the reactions in question, the tricarballylic acids could not be obtained sufficiently pure for our purposes. The hydrolysed products of such experiments were always oily acids, which crystallised very slowly, and even when crystalline acids were finally isolated, analyses indicated that they contained small amounts of, probably, ethoxy-acids, which could not be entirely eliminated by repeated recrystallisations from suitable solvents. We therefore sought for some liquid other than alcohol as the diluting medium for the main reaction. Xylene was first tried, but the sodium compounds of the cyanosuccinates proved too insoluble in it; toluene seemed more promising, and after many trials we finally devised the following mode of procedure, which completely obviated the difficulties above indicated.

Interaction of Ethyl Sodiocyanosuccinates and Bromo-fatty Esters in Toluene Solution.

The sodium compound of the cyanosuccinic ester was first prepared in the usual manner by adding the ester to the calculated quantity of sodium ethoxide dissolved in alcohol. It is convenient to work with one-eighth gram-molecular proportions of the cyanosuccinic ester in each separate experiment. The excess of alcohol was then distilled in a current of dry hydrogen until a thermometer immersed in the liquid showed a temperature of 120°; the sodium compound of the cyanosuccinic ester was thus left in a viscous, pasty condition, sometimes slightly charred, but quite free from alcohol. About 50 c.c. of chloroform were then added and the mixture heated in a reflux apparatus on the water-bath, until the sodium compound had entirely dissolved. To the cooled solution were successively added (1) the calculated quantity of the α-bromo-fatty ester, and (2) 100 c.c. of pure toluene mixed with 5 or 10 c.c. of xylene. The whole was thoroughly shaken, after which the chloroform was distilled in a current of dry hydrogen, the distillation being continued until a thermometer inserted in the liquid showed a temperature of 105°. The residual liquid was poured while still hot into Carius tubes; after displacing air by dry carbon dioxide the tubes were sealed and then heated to 150—180° for five or six hours. The precise temperature required must be determined by trial in each particular case; the limits between the temperature at which the reaction proceeds satisfactorily and that at which charring begins being somewhat narrow. The cooled liquid was poured into excess of water, and the oil which separated was isolated by means of ether. The ether and toluene were then evaporated at atmospheric pressure (up to 120—130°), and the residual dark brown oil afterwards fractionated under a pressure of 25 to 30 mm. The fractions which distilled below 190° consisted mainly of unchanged cyanosuccinic ester, together with some bromo-fatty ester. The cyanotricarballylate distilled between 195° and 215° as a viscous, nearly colourless oil, the greater part of which boiled between 200° and 205°. The yields were from 19 to 20 per cent. of the theoretical. The oils were subsequently hydrolysed by boiling with concentrated hydrochloric acid for three to four days, and the acids isolated from the hydrolytic products as described by Bone and Sprankling (*loc. cit.*).

$\alpha\alpha\gamma$-*Trimethyltricarballylic Acid*,

$$CO_2H\cdot CMe_2\cdot CH(CO_2H)\cdot CHMe\cdot CO_2H.$$

—(*a*). From the hydrolysed product of the interaction of ethyl-$\beta\beta$-dimethylcyanosuccinate and ethyl α-bromopropionate we isolated an acid which in the crude state melted at 123—125°, but after several recrystallisations from chloroform quite sharply at 133—134°. Analysis indicated that it was a tribasic acid:

0·1620 gave 0·2940 CO_2 and 0·0994 H_2O. C = 49·55; H = 6·78.

$C_9H_{14}O_6$ requires C = 49·5; H = 6·42 per cent.

0·1800 of silver salt gave 0·1086 Ag. Ag = 60·4.

$C_9H_{11}O_6Ag_3$ requires Ag = 60·1 per cent.

The acid was very soluble in water, alcohol, or ether; only moderately so in chloroform and insoluble in light petroleum. It is best purified by crystallisation from chloroform.

Dissociation Constant.—Conductivity determinations for four successive dilutions at 25° gave the following results:

v.	μ_v.	m.	$K = 100k$.
27	21·51	0·0597	0·01403
54	30·35	0·0843	0·01437
108	42·58	0·1183	0·01462
216	59·45	0·1651	0·01510

K = 0·0145.

Whilst this value is of the same order of magnitude as those of other tricarballylic acids, it is much lower than that of either tricarballylic acid itself (0·022), or those of its mono- or di-methyl derivatives.

Anhydro-acid.—When boiled with acetyl chloride the acid yielded a liquid anhydro-acid, which, although distilled in a vacuum, did not solidify; in this respect it resembles the anhydro-acids of the two α-methyltricarballylic acids already described by Bone and Sprankling. With water the liquid yielded the original acid, melting at 133°.

Calcium Salt.—As in the case of the other tricarballylic acids, a crystalline calcium salt immediately separated when a solution of the ammonium salt was boiled with calcium chloride solution; the precipitate was permanent and did not appreciably redissolve on cooling.

Analyses of the salt dried at 100° established the formula $(C_9H_{11}O_6)_2Ca_3,H_2O$.

Since $\alpha\alpha\gamma$-trimethyltricarballylic acid contains two asymmetric carbon atoms it should exist in two inactive stereoisomeric forms; on the other hand, the molecule of the $\alpha\alpha\gamma\gamma$-tetramethyl acid is symmetrical, and therefore in its case the possibility of stereoisomerism is precluded.

All attempts to convert the $\alpha\alpha\gamma$-trimethyltricarballylic acid into a stereoisomeride entirely failed; it underwent no appreciable change when heated under pressure with strong hydrochloric acid at 220° for eight hours, except that it was converted into the liquid anhydro-acid, which with water yielded the original acid melting at 134—135°. Further, we were unable to isolate any stereoisomeride from the hydrolysed product of the interaction of ethyl methylsodiocyanosuccinate and ethyl bromo*iso*butyrate.

αδ-Dimethylbutane αβδ-tricarboxylic Acid,

$$CO_2H\cdot CHMe\cdot CH(CO_2H)\cdot CH_2\cdot CHMe\cdot CO_2H.$$

(*b*) From the hydrolysed product of the interaction of ethyl methylsodiocyanosuccinate and ethyl α-bromo*iso*butyrate we obtained a tribasic acid isomeric with that just described; the crude acid melted at 100—102°, but after crystallisation from chloroform and light petroleum at 107°. On analysis:

0·1260 gave 0·2281 CO_2 and 0·0760 H_2O. C = 49·37; H = 6·70.

$C_9H_{14}O_6$ requires C = 49·5; H = 6·42 per cent.

0·1160 silver salt gave 0·0792 CO_2; 0·0238 H_2O and 0·0664 Ag; C = 19·64; H = 2·40; Ag = 60·36.

$C_9H_{11}O_6Ag_3$ requires C = 20·00; H = 2·40; Ag = 60·10 per cent.

Its solubilities in alcohol, ether, chloroform or light petroleum resembled those of the isomeric acid (m. p. 134°); its dissociation constant at 25° was determined as follows:

v.	μ_v.	m.	$K = 100\,k$.
83·52	39·09	0·1086	0·0158
167·04	53·67	0·1491	0·0156
334·08	75·92	0·2109	0·0168
668·16	100·36	0·2788	0·0161

The constant is 0·0161.

Anhydro-acid.—With acetyl chloride the acid yielded the corresponding liquid anhydride; this with water regenerated the original acid:

0·1301 gave 0·2569 CO_2 and 0·0710 H_2O. C = 53·89; H = 6·07.

$C_9H_{12}O_5$ requires C = 54·00; H = 6·07 per cent.

At first we concluded that the two isomeric acids just described represented respectively the two possible inactive forms of *ααγ*-trimethyltricarballylic acid, although it seemed curious that one acid only should be produced in each of two so nearly allied reactions, and that the same acid should be always produced as the result of the same reaction.

The next question was to find whether one acid can be converted into the other by any of the methods which have been used in the case of other stereoisomeric tricarballylic acids. We have already shown that the acid melting at 134° exhibited no sign of stereoisomeric change, either after prolonged treatment with strong hydrochloric acid or with acetic anhydride, at high temperatures. Experiments with the acid melting at 107° were equally without result in this respect, although we heated it with strong hydrochloric acid to 230° for twelve hours. These negative results, whilst not conclusively proving that the two acids are not stereoisomerides, certainly suggest that they are structurally different.

An examination of the calcium salt of the acid (m. p. 107°) strengthened this conclusion. The calcium salts of all the other known methyl-substituted tricarballylic acids are immediately precipitated, when solutions of their ammonium salts are boiled with calcium chloride, although some of them redissolve on cooling. The calcium salt of the acid, melting at 133—134°, was in this way instantly precipitated, and it did not redissolve on cooling. In contrast with this behaviour, the acid melting at 107° yielded no insoluble calcium salt, and, moreover, the melting point of the acid is 30° lower than those of all the other methyltricarballylic acids.

In considering the mechanism of the reaction between ethyl *α*-bromo*iso*butyrate and methyl sodiocyanosuccinate, it seemed probable that first of all hydrogen bromide is eliminated from the ethyl *α*-bromo*iso*butyrate, and that the resulting methylacrylic ester subsequently condenses with the ethyl methylsodiocyanosuccinate as follows:

$$\begin{aligned}&\mathrm{CO_2Et{\cdot}CHMe{\cdot}CNa(CN){\cdot}CO_2Et + CH_2{:}CMe{\cdot}CO_2Et} \longrightarrow \\ &\qquad\qquad \mathrm{CO_2Et{\cdot}CHMe{\cdot}C(CH_2{\cdot}CMeNa{\cdot}CO_2Et)(CN){\cdot}CO_2Et.}\end{aligned}$$

The product of the reaction would, on hydrolysis, yield *αδ*-dimethylbutane *αβδ*-tricarboxylic acid,

$$\mathrm{CO_2H{\cdot}CHMe{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H.}$$

This supposition was confirmed by condensing methyl sodiocyanosuccinic ester with monomethylacrylic ester; on hydrolysing the condensation product with hydrochloric acid, we obtained an acid identical in all respects with the acid melting at 107°.

The sodium compound of the methyl cyanosuccinic ester was prepared by adding the ester to the calculated quantity of sodium ethoxide dissolved in alcohol. To this was added the calculated amount of methylacrylic ester (prepared by Thorpe's method, Trans., 1900, 77, 947), and the mixture boiled for sixteen hours on the water-bath. The product, which had darkened in colour, was cooled and poured into water, when a brown oil was obtained, which was extracted with ether in the usual manner. After evaporating the ether the residual oil was fractionated under a pressure of 40 mm.; the fraction collected between 190° and 205° was hydrolysed by boiling with concentrated hydrochloric acid for sixteen hours in a reflux apparatus, and the acid isolated as described by Bone and Sprankling (*loc. cit.*). The acid was at first obtained as a pale yellow oil, which solidified on standing for some hours in a vacuous desiccator. On crystallisation from chloroform it yielded small white crystals, which melted at 105°. A mixture in equal proportions of this and the acid (m. p. 107°) prepared from the bromo-fatty ester melted at 104—105°.

This acid gave no insoluble calcium salt when a solution of its ammonium salt was boiled with a solution of calcium chloride. Its solution in water does not decolorise alkaline permanganate in the cold.

Its solubilities in water, ether, alcohol, chloroform or light petroleum agree with those of the acid melting at 107°.

0·1471 gave 0·2657 CO_2 and 0·0870 H_2O ; $C = 49·25$; $H = 6·59$.

$C_9H_{14}O_6$ requires $C = 49·5$; $H = 6·42$ per cent.

0·1540 *silver* salt gave 0·0930 Ag. $Ag = 60·38$.

$C_9H_{11}O_6Ag_3$ requires $Ag = 60·10$ per cent.

The conductivity for four dilutions was determined, and gave results closely agreeing with those of the acid melting at 107°.

v.	μ_v.	m.	$K = 100k$.
43·4	27·68	0·0769	0·01476
86·8	38·99	0·1080	0·01506
173·6	54·55	0·1510	0·01547
347·2	75·30	0·2090	0·01590

The constant is 0·01530.

It will, therefore, be seen that this acid agrees in all its properties with that prepared by the first method given in this paper, and is therefore identical with it. The structural formula follows from the synthesis, showing that the acid is not a trimethyltricarballylic acid, although isomeric with this group of acids.

ααγγ-*Tetramethyltricarballylic Acid*,
$CO_2H\cdot CMe_2\cdot CH(CO_2H)\cdot CMe_2\cdot CO_2H$.

This acid was isolated from the hydrolysed product of higher boiling point (190—215°/35 mm.), obtained by the interaction of ethyl ββ-dimethylsodiocyanosuccinate and ethyl α-bromo*iso*butyrate in toluene solution. After two recrystallisations from chloroform it melted at 140°. On analysis :

0·1628 gave 0·3046 CO_2 and 0·1026 H_2O. $C = 51·31$; $H = 7·03$.

$C_{10}H_{16}O_6$ requires $C = 51·70$; $H = 6·94$ per cent.

0·2110 *silver* salt gave 0·1244 Ag. Ag = 58·95.
$C_{10}H_{13}O_6Ag_3$ requires Ag = 58·6 per cent.

The *calcium* salt, dried at 100°, had the composition
$(C_{10}H_{13}O_6)_2Ca_3,\frac{1}{2}H_2O$.
The acid crystallises well from chloroform, is very soluble in water, alcohol, ether, or benzene, but is insoluble in light petroleum. Its dissociation constant was determined.

v.	μ_v.	*m*.	*K* = 100*k*.
34·4	24·80	0·0688	0·01478
68·8	34·40	0·0970	0·01514
137·6	48·00	0·1333	0·01500
275·2	66·66	0·1850	0·01527

The constant is 0·01505.

Anhydro-acid.—With acetyl chloride the acid yielded the corresponding liquid anhydro-acid, which on standing several days in a vacuous desiccator solidified to a white crystalline substance melting at 132°; this with water regenerated the original acid melting at 139°.

The authors wish to express their best thanks to Prof. Bone for his kind assistance in the earlier stages of the research and also to the Research Fund Committee of the Chemical Society for a grant, which enabled them to purchase the more expensive chemicals used in the work.

THE VICTORIA UNIVERSITY OF MANCHESTER.

XXXIX.—*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part VI. The Partially Methylated* 4 : 6-*Diamino*-m-*xylenes.*

By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

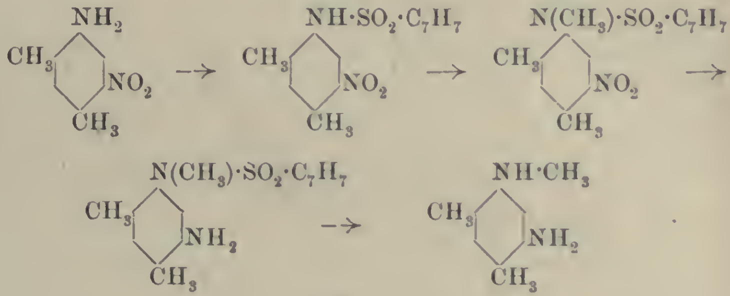
IT was previously shown by one of the authors that aminoazo-compounds can be obtained from diazonium salts and 4 : 6-diamino-*m*-xylene, whereas this condensation is entirely inhibited when the aminic hydrogen atoms are completely replaced by alkyl groups as in tetramethyl-4 : 6-diamino-*m*-xylene (Trans., 1902, 81, 89, 656).

As the partially methylated bases of this series had not been propared, it seemed of interest to obtain these substances in order to ascertain how the progressive methylation of the primary diamine would affect the formation of azo-derivatives.

One of these partially methylated bases, namely, *s*-dimethyl-4 : 6-diamino-*m*-xylene, was recently prepared and studied by one of the authors and Mr. A. Clayton (Trans., 1906, **89**, 1054), when it was found that the combination with diazo-compounds proceeded with great difficulty, and the product appeared to contain both a diazoamine and an aminoazo-compound.

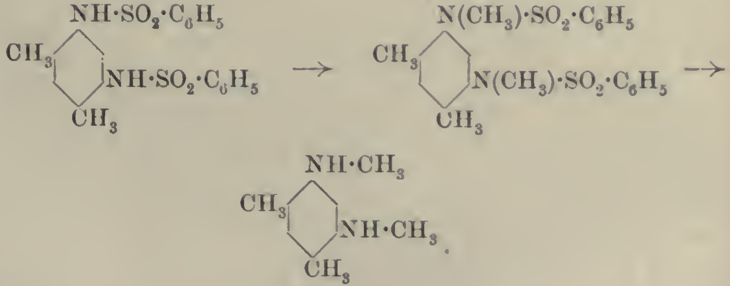
All the other partially methylated derivatives of 4 : 6-diamino-*m*-xylene, namely, *methyl*-4 : 6-*diamino*-m-*xylene*, as-*dimethyl*-4 : 6-*diamino*-m-*xylene* and *trimethyl*-4 : 6-*diamino*-m-*xylene*, have now been obtained by methods described in the experimental part of this communication, and, as will be seen from the following diagram, the processes employed were devised to yield as far as possible the required base uncontaminated by other members of the series :

A.



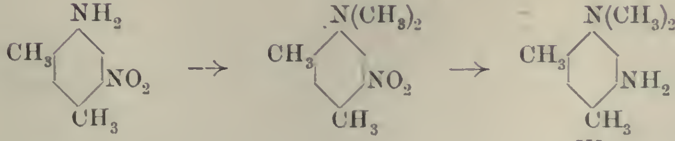
I.

B.



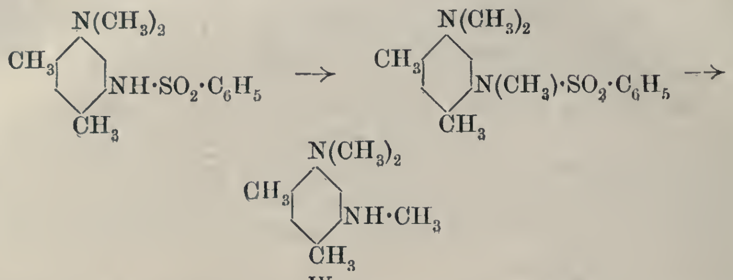
II.

C.



III.

D.



IV.

These diamines were readily characterised by their behaviour towards nitrous acid, each furnishing a product of a different type. Methyl-4 : 6-diamino-*m*-xylene (I) gave a nitroso-diazonium salt, *as*-dimethyl-4 : 6-diamino-*m*-xylene (III) formed a normal diazonium salt, whilst trimethyl-4 : 6-diamino-*m*-xylene (IV) gave rise to a mononitrosoamine. *s*-Dimethyl-4 : 6-diamino-*m*-xylene (II), previously examined, yielded a dinitrosoamine (Morgan and Clayton, *loc. cit.*).

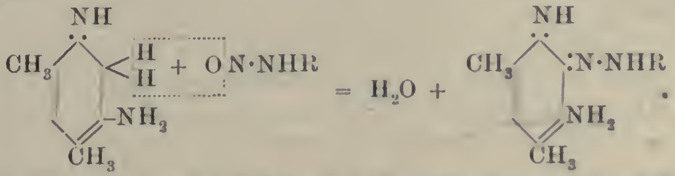
These partially methylated diamines were now submitted in turn to the action of various diazonium salts.

Methyl-4 ; 6-diamino-*m*-xylene, like 4 : 6-diamino-*m*-xylene itself, furnished only azo-derivatives, but the yields in this case were even smaller than with the unmethylated base, and diazoamines were not isolated.

as-Dimethyl-4 : 6-diamino-*m*-xylene, on treatment with *p*-nitrobenzenediazonium chloride, furnished a well-defined diazoamine, accompanied only by traces of an azo-derivative. This *as*-dimethyl base may be compared with *s*-dimethyl-4 : 6-diamino-*m*-xylene which, with the same diazonium salt, gave rise to a mixture of azo-derivative and diazoamine (Morgan and Clayton, *loc. cit.*).

Trimethyl-4 : 6-diamino-*m*-xylene combined readily with diazotised amines to form well-defined diazoamines accompanied only by traces of azo-derivatives. The diazoamines produced with *p*-nitrobenzenediazonium and toluene-*p*-diazonium chlorides respectively were crystallisable compounds easily isolated in a state of purity and constituting the main product of the condensation.

The experiments on the dipara-substituted *m*-diamines have thus shown that progressive methylation of these bases renders increasingly difficult the formation of *o*-aminoazo-compounds, and that complete methylation altogether prevents this condensation. Now this tendency is entirely absent in the *p*-aminoazo-series where the completely methylated bases form azo-derivatives just as readily as the primary diamines. This striking contrast points to some difference in the mode of formation of the two series of azo-compounds. The presence of a labile aminic hydrogen atom seems to be essential for the production of an ortho-aminoazo-compound, and this circumstance suggests the view that the condensation actually occurs with a dynamic form of the diamine in which an ortho-quinonoid configuration has been acquired.



The system may then revert more or less completely to the benzenoid form after condensation has been effected.

EXPERIMENTAL.

Methyl-4 : 6-*diamino*-m-*xylene*.

m-Xylene was nitrated by adding to 250 grams of the hydrocarbon cooled by salt and ice, a mixture of 500 grams of concentrated sulphuric acid and 575 grams of nitric acid (sp. gr. 1·52). The mixture was subsequently heated for one hour on the water-bath, and then cooled and poured on to ice. The 4 : 6-dinitro-*m*-xylene was isolated by repeatedly crystallising the product from alcohol, taking at each stage the less soluble crop of crystals.

6-Nitro-4-amino-*m*-xylene was prepared by dissolving the dinitro-compound (20 grams) in 120 c.c. of warm alcohol, adding 10 c.c. of strong ammonia, and saturating the solution with hydrogen sulphide; the addition of ammonia and hydrogen sulphide was repeated after half an hour's heating, and finally, when a considerable amount of a crystalline yellow solid had separated, a small quantity of water was added, and the alcohol was evaporated. The nitro-base was extracted with hydrochloric acid from the washed residue and reprecipitated from the filtered solution by ammonia; the crude product melted at 120°, and was recrystallised until the correct melting point (123°) was obtained.

Toluene-p-*sulphonyl*-6-*nitro*-4-*amino*-m-*xylene*,

$$NO_2\cdot C_6H_2(CH_3)_2\cdot NH\cdot SO_2\cdot C_7H_7,$$

was obtained by heating for twenty hours in dry pyridine 20 grams of the nitroxylidine and an excess of toluene-*p*-sulphonic chloride (43 grams); the yield amounted to 33 grams, and the product after crystallisation from alcohol separated in transparent, pale yellow crystals melting at 192°:

0·3716 gave 28·4 c.c. nitrogen at 18° and 756 mm. N = 8·78.

$C_{15}H_{16}O_4N_2S$ requires N = 8·70 per cent.

Toluene-p-*sulphonyl*-6-*nitro*-4-*methylamino*-m-*xylene*,

$$NO_2\cdot C_6H_2(CH_3)_2\cdot N(CH_3)\cdot SO_2\cdot C_7H_7,$$

obtained by methylating the preceding compound in a reflux apparatus with methyl iodide and alcoholic soda, separated from alcohol in colourless, prismatic crystals (m. p. 135—136°) which are insoluble in aqueous alkalis:

0·1996 gave 14·6 c.c. nitrogen at 20° and 778 mm. N = 8·57.

$C_{16}H_{18}O_4N_2S$ requires N = 8·38 per cent.

4-*Toluene*-p-*sulphonyl*-4-*methyl*-4 : 6-*diamino*-m-*xylene*,

$$NH_2\cdot C_6H_2(CH_3)_2\cdot N(CH_3)\cdot SO_2\cdot C_7H_7,$$

was produced by reducing the preceding nitro-compound with iron and dilute acetic acid, but as it did not crystallise satisfactorily from the ordinary organic media it was converted into its *hydrochloride*, which separates from an acid solution in almost colourless prisms melting at 225°:

0·4426 gave 0·1752 AgCl. Cl = 9·96.

$C_{16}H_{20}O_2N_2S,HCl$ requires Cl = 10·42 per cent.

The base yields a very insoluble platinichloride and an *acetyl* derivative, crystallising from benzene in colourless, felted needles, and melting at 176°.

The *azo-β-naphthol* derivative,

$$C_7H_7\cdot SO_2\cdot N(CH_3)\cdot C_6H_2(CH_3)_2\cdot N_2\cdot C_{10}H_6\cdot OH,$$

crystallises from alcohol or acetic acid in bright red, felted needles, and melts at 177—178°.

Hydrolysis of the Sulphonamide.—This operation was successfully effected by heating for three hours at 120—130° a large number of sealed tubes, each containing 3·5 grams of the crystalline hydrochloride of the sulphonamide and 12 c.c. of concentrated hydrochloric acid. The product was rendered alkaline with ammonia and extracted with chloroform, the extract being then dried with anhydrous sodium sulphate and evaporated on the water-bath. The dark, oily residue thus obtained was distilled under diminished pressure in a current of carbon dioxide, when a colourless oil passed over at 180°/25—30 mm. This fraction when redistilled boiled constantly at 166—167°/10 mm., and solidified in the receiver in stellate clusters of colourless hastate crystals melting at 57°:

0·1739 gave 0·4550 CO_2 and 0·1503 H_2O. C = 71·35; H = 9·60.
0·1892 ,, 0·4978 CO_2 ,, 0·1619 H_2O. C = 71·75; H = 9·50.
0·1521 ,, 24·6 c.c. nitrogen at 19° and 763 mm. N = 18·68.

$C_9H_{14}N_2$ requires C = 72·00; H = 9·33; N = 18·66 per cent.

This diamine, which is extremely oxidisable, does not crystallise readily from the ordinary organic solvents, but its benzene solution on evaporation deposits transparent, colourless plates. When the hydrochloride of this base is treated with excess of sodium nitrite it reacts with two molecular proportions of nitrous acid, forming a soluble nitrosodiazonium chloride; this substance condenses with alkaline β-naphthol to yield an *azo-β-naphthol* derivative,

$$NO\cdot N(CH_3)\cdot C_6H_2(CH_3)_2\cdot N_2\cdot C_{10}H_6\cdot OH,$$

which separates from benzene in lustrous, red prisms or lath-like crystals, melting at 195—196°:

0·1720 gave 0·4337 CO_2 and 0·0937 H_2O. C = 68·76; H = 6·05.
0·1332 „ 20·2 c.c. nitrogen at 20° and 773 mm. N = 17·66.
$C_{19}H_{18}O_2N_4$ requires C = 68·26; H = 5·38; N = 16·76 per cent.

This substance was analysed only with difficulty owing to the readiness with which it evolves nitrous fumes on heating.

as-*Dimethyl*-4 : 6-*diamino*-m-*xylene*.

Methylation of 6-*Nitro*-4-*amino*-m-*xylene*.—The recrystallised nitroxylidine (m. p. 123°) was converted into its hydrobromide, and 3 grams of this salt were heated with 12 c.c. of methyl alcohol for five hours at 150—180°, the most suitable temperature being 160°. The sealed tubes then contained a clear red solution quite free from tar. The contents of sixty tubes were diluted with water, boiled with animal charcoal, and then rendered ammoniacal. The methylated nitroxylidine, which was extracted with chloroform, refused to solidify on evaporating off the solvent and cooling the residue. A small portion was converted into its crystalline *picrate*, $NO_2\cdot C_6H_2(CH_3)_2\cdot N(CH_3)_2,C_6H_2(NO_2)_3\cdot OH$, which melts with violent decomposition at 170—173°:

0·1174 gave 16·4 c.c. nitrogen at 20° and 777 mm. N = 16·39.
$C_{16}H_{17}O_9N_5$ requires N = 16·54 per cent.

The main bulk of the oily nitro-base was reduced with a moderate excess of tin and hydrochloric acid; the metal was subsequently removed with hydrogen sulphide and the solution of the hydrochloride of the methylated diamine evaporated to a syrupy consistence. The base set free with ammonia was extracted with chloroform containing a small quantity of ether; the extract after drying with anhydrous sodium sulphate was evaporated at 100°, and the oily residue distilled under diminished pressure, when a viscid, yellow oil passed over at 174°/45 mm. When redistilled in a current of carbon dioxide the oil boiled constantly at 149—150°/21 mm. and was obtained quite colourless:

0·2328 gave 0·6242 CO_2 and 0·2108 H_2O. C = 73·13; H = 10·06.
0·1470 „ 21·6 c.c. nitrogen at 18° and 769 mm. N = 17·19.
$C_{10}H_{16}N_2$ requires C = 73·17; H = 9·75; N = 17·07 per cent.

as-*Dimethyl*-4 : 6-*diamino*-m-*xylene* rapidly assumes a yellow colour on exposure to the atmosphere and ultimately becomes red; it has a faint but characteristic odour and does not solidify at – 10°. Its salts with the mineral acids are fairly soluble in water; its *benzoyl* derivative, $N(CH_3)_2\cdot C_6H_2(CH_3)_2\cdot NH\cdot CO\cdot C_6H_5$, crystallises from a mixture of absolute alcohol and light petroleum (b. p. 60—80°) in colourless, glistening plates and melts at 123°.

When treated with excess of sodium nitrite in acid solution the hydrochloride of this diamine reacts with only one molecular proportion of nitrous acid, yielding a soluble diazonium salt which condenses with β-naphthol to form the *azo-β-naphthol* derivative,

$$N(CH_3)_2\cdot C_6H_2(CH_3)_2\cdot N_2\cdot C_{10}H_6\cdot OH,$$

which separates from benzene in stellate clusters of prismatic crystals melting at 140—142°.

0·1883 gave 21·5 c.c. nitrogen at 19° and 763 mm. N = 13·19.
$C_{20}H_{21}ON_3$ requires N = 13·16 per cent.

Trimethyl-4 : 6-*diamino*-m-*xylene.*

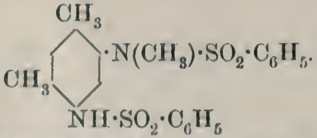
Benzenesulphonyl-as-*dimethyl*-4 : 6-*diamino*-m-*xylene*,

$$N(CH_3)_2\cdot C_6H_2(CH_3)_2\cdot NH\cdot SO_2\cdot C_6H_5.$$

—This sulphonamide was obtained from *as*-dimethyl-4 : 6-diamino-*m*-xylene and benzenesulphonic chloride by the Schotten-Baumann reaction. The main bulk of the product dissolved in the aqueous caustic soda, although a small amount of a substance insoluble in the alkali was isolated. This compound, which crystallised from alcohol or benzene in colourless, transparent plates, melted at 113—115° and contained 9·38 per cent. of nitrogen; it was not, however, further examined. The alkaline solution, when acidified with excess of hydrochloric acid, yielded (*a*) a small quantity of insoluble matter; this product when crystallised from alcohol separated in hard, colourless prisms and melted at 136—138°:

0·2690 gave 15 c.c. nitrogen at 19° and 780 mm. N = 6·56.
$C_{21}H_{22}O_4N_2S_2$ requires N = 6·51 per cent.

This compound appeared to be derived from a small quantity of methyl-4 : 6-diamino-*m*-xylene present in the dimethyl base and its properties (solubility in alkali hydroxides and insolubility in acids) pointed to the formula



CH_3
$\cdot N(CH_3)\cdot SO_2\cdot C_6H_5$.
CH_3
$NH\cdot SO_2\cdot C_6H_5$

This supposition was confirmed by applying the Schotten-Baumann reaction to methyl-4 : 6-diamino-*m*-xylene when the same compound was produced.

The main hydrochloric acid solution (*a*), after filtration from the preceding compound, was treated with excess of sodium acetate, when the required benzenesulphonyl-*as*-dimethyl-4 : 6-diamino-*m*-xylene was obtained as a snow-white precipitate; this crystallised from alcohol and was obtained in colourless needles melting at 112—113°:

0·3170 gave 25·2 c.c. nitrogen at 17·5° and 771 mm. N = 9·33.
$C_{16}H_{20}O_2N_2S$ requires N = 9·21 per cent.

Benzenesulphonyltrimethyl-4 : 6-*diamino*-m-*xylene*,
$N(CH_3)_2 \cdot C_6H_2(CH_3)_2 \cdot N(CH_3) \cdot SO_2 \cdot C_6H_5$,
was prepared from the preceding compound by heating it with methyl iodide and alcoholic potash in a reflux apparatus for nine hours. The product, which was quite insoluble in aqueous caustic soda, was dissolved in warm dilute hydrochloric acid, reprecipitated from the filtered solution by either sodium acetate or ammonia, and crystallised from alcohol, when it separated in transparent, lustrous, colourless needles melting at 122—123°:

0·2216 gave 17·5 c.c. nitrogen at 20° and 779 mm. N = 9·26.
$C_{17}H_{22}O_2N_2S$ requires N = 8·80 per cent.

Hydrolysis of the Trimethylated Sulphonamide.—Several tubes were each charged with 3 grams of the sulphonamide and 12 c.c. of concentrated hydrochloric acid and heated at 130—150° for four hours. A clear red solution was generally obtained, although in a few instances a small amount of tar was present. The filtered liquid was rendered ammoniacal and extracted with chloroform; the oily residue left after evaporating the dehydrated extract at 100° was distilled under diminished pressure in a current of carbon dioxide. The main portion boiled at 151°/20 mm. and when rectified at 145°/15 mm. was obtained as a colourless oil which slowly solidified to a mass of colourless crystals melting at 40—42°:

0·1432 gave 0·3864 CO_2 and 0·1321 H_2O; C = 73·60; H = 10·25.
0·1414 „ 18·8 c.c. nitrogen at 16° and 775 mm. N = 15·81.
$C_{11}H_{18}N_2$ requires C = 74·15; H = 10·11; N = 15·73 per cent.

Trimethyl-4 : 6-*diamino*-m-*xylene*, when treated in cold dilute hydrochloric acid with excess of sodium nitrite, yielded only a mononitrosoamine which separated on the addition of excess of sodium acetate as an oil which slowly solidified to a mass of almost colourless crystals melting at 45°; 1 gram of the diamine furnished one gram of its *nitrosoamine*:

0·1428 gave 25·0 c.c. nitrogen at 16° and 775 mm. N = 20·82.
$C_{11}H_{17}ON_3$ requires N = 20·28 per cent.

This nitrosoamine gave intense colorations in all the phases of the Liebermann reaction.

Action of Diazonium Salts on the Partially Methylated 4:6-*Diamino*-m-*xylenes.*

(1) *Methyl*-4 : 6-*diamino*-m-*xylene.*—A comparative dye-test made with diazotised primuline on the cotton fibre showed that this base behaved like 4 : 6-diamino-*m*-xylene itself towards this diazo-compound, the shades of red produced being very similar in hue and intensity. On treating the new diamine with the simpler diazonium salts it was found extremely difficult to isolate any well-defined condensation products. The substances obtained by means of toluene-*p*-diazonium chloride were tarry, whilst with *p*-nitrobenzenediazonium chloride only a very small yield of any solid azo-derivative was isolated; in neither case was any diazoamine obtained. On adding a solution of the latter diazonium salt to one of the diamine and then treating the mixture with aqueous sodium acetate, a deep brown precipitate appeared, which was accompanied by frothing. This product was collected after twelve hours, and, when dry, extracted with alcohol. A small quantity of a brownish-purple, crystalline substance separated from the alcoholic solution. This product, which contained chlorine, gave an intense reddish-brown coloration with concentrated sulphuric acid, and behaved as the hydrochloride of the azo-compound, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H(CH_3)_2(NH_2)\cdot NH\cdot CH_3$.

0·1432 gave 24·6 c.c. nitrogen at 20° and 778 mm. N = 20·14.

$C_{15}H_{17}O_2N_5,HCl$ requires N = 20·86 per cent.

This hydrochloride melted at 199—202°.

(2) as-*Dimethyl*-4 : 6-*diamino*-m-*xylene.*—The primuline dye-test indicated a marked diminution in the intensity of the ingrain azo-colouring matter obtained by using this diamine as developer. A comparative experiment made with *s*-dimethyl-4 : 6-diamino-*m*-xylene showed that the two isomerides give colours of similar hue and intensity.

A condensation of the diamine and *p*-nitrobenzenediazonium chloride effected in the presence of excess of aqueous sodium acetate led to the production of a diazoamine. This compound, which separated as a brownish-yellow precipitate, was obtained in almost quantitative yield, 3·3 grams of the diamine, and 2·76 grams of *p*-nitroaniline, furnishing 5·5 grams of this product. This diazoamine was either decomposed or not dissolved by the available solvents, and was therefore prepared from carefully purified materials and analysed after drying for some days over concentrated sulphuric acid:

0·1784 gave 35·0 c.c. nitrogen at 19° and 751 mm. N = 22·34.
$C_{16}H_{19}O_2N_5$ requires N = 22·36 per cent.

A weighed portion, when heated with concentrated hydrochloric acid in the gas-volumeter, evolved the whole of its diazo-nitrogen:

0·4138 gave 29·0 c.c. nitrogen at 17° and 751 mm. N = 8·03.
$C_{16}H_{19}O_2N_5$ requires diazo-N = 8·91 per cent.

These results show that this substance is p-*nitrobenzenediazo*-as-*dimethyl*-4 : 6-*diamino*-m-*xylene*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_2(CH_3)_2\cdot N(CH_3)_2.$$

With alcoholic potash it developed the intense purple coloration characteristic of a diazoamine obtained from *p*-nitroaniline and a primary base; it melted with violent decomposition at 135—140°.

Several attempts were made to transform the diazoamine into the isomeric azo-derivative by warming with the hydrochloride of the diamine in alcoholic solutions and also in solutions of the diamine itself, but in neither case was this change effected. When *as*-dimethyl-4 : 6-diamino-*m*-xylene was treated with toluene-*p*-diazonium chloride in the presence of aqueous sodium acetate, a migration of the diazo-group occurred, with the result that a portion of the diamine became diazotised and then gave rise to tarry phenolic products soluble in caustic soda whilst diazoamino-*p*-toluene (m. p. 116—118°) was produced. The identity of this diazoamine was confirmed by analysis (N = 18·47, theory requires N = 18·60) and by decomposing it with cold concentrated hydrochloric acid and then condensing the resulting diazonium salt with β-naphthol: the latter compound melted at 132°, the correct value being 134—135°.

This symmetrical diazoamine was not, however, the only product; a certain amount of viscid material was obtained which was insoluble in aqueous alkalis but gave intense red colorations with concentrated hydrochloric and sulphuric acids. These reactions pointed to the presence of an azo-derivative but the substance could not be isolated in a definite form.

(3) *Trimethyl*-4 : 6-*diamino*-m-*xylene*.—The primuline experiment showed that this diamine had only a very slight tendency to form an ingrain azo-colouring matter. This indication was confirmed by the results obtained with simpler diazonium salts, when diazoamines were obtained almost exclusively.

p-*Nitrobenzenediazotrimethyl*-4 : 6-*diamino*-m-*xylene*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_2(CH_3)_2\cdot N(CH_3)_2.$$

This diazoamine separates as a viscid, brownish red precipitate on condensing the diamine and *p*-nitrobenzenediazonium chloride in aqueous sodium acetate. When dried and freed from by-products by washing with cold alcohol, it was crystallised from this medium and separated in reddish-yellow crystals having a violet reflex:

0·1976 gave 36·2 c.c. nitrogen at 20° and 778 mm. N = 21·46.
0·1326 „ 0·3028 CO_2 and 0·0742 H_2O; C = 62·27; H = 6·22.
$C_{17}H_{21}O_2N_5$ requires N = 21·40; C = 62·38; H = 6·45 per cent.

This diazoamine melted with violent decomposition at 108—115°; it gave no coloration either with cold concentrated sulphuric acid or with alcoholic potash. These negative results indicate respectively an absence of azo-compound or of nitro-diazoamine derived from a primary base. When decomposed with concentrated hydrochloric acid in the gas-volumeter the new diazoamine evolved two-fifths of its nitrogen, a result which corroborates the above view of its constitution.

The alcoholic washings from the crude diazoamine on partial evaporation yielded a dark red, semi-crystalline residue which developed an intense brownish-red coloration with cold concentrated sulphuric acid. This product probably contained an azo-compound but the amount present was too small for more detailed examination:

Toluene-p-*diazotrimethyl*-4 : 6-*diamino*-m-*xylene*,

$$CH_3 \cdot C_6H_4 \cdot N_2 \cdot N(CH_3) \cdot C_6H_2(CH_3)_2 \cdot N(CH_3)_2.$$

—Trimethyl-4 : 6-diamino-*m*-xylene, when condensed in the usual manner with toluene-*p*-diazonium chloride, slowly furnished a yellowish-red, viscid precipitate which, when collected and washed with a little cold alcohol, yielded the crude diazoamine. This substance was purified for analysis by dissolving in light petroleum (b. p. 60—80°) and adding to the solution a small quantity of alcohol, when a precipitate of yellowish-white plates was obtained which melted at 70—71°:

0·1034 gave 0·2782 CO_2 and 0·0719 H_2O; C = 73·36; H = 7·73.
0·1230 „ 19·6 c.c. nitrogen at 20° and 777 mm. N = 18·71.
$C_{18}H_{24}N_4$ requires C = 72·97; H = 8·10; N = 18·91 per cent.

The diazoamine readily underwent fission with cold hydrochloric acid, regenerating the diamine and the toluene-*p*-diazonium chloride; the latter was identified by means of its azo-β-naphthol derivative (m. p. 134—135°). All attempts to transform the two foregoing diazoamines into the isomeric azo-derivatives proved unavailing.

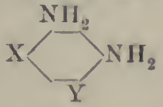
Summary of the Interactions of Aromatic Meta-diamines and Diazo-compounds.

As the investigation described in this paper completes the survey of the interactions of meta-diamines and diazonium salts in a large number of representative cases, it becomes possible to summarise the conclusions which may be drawn from these researches.*

1. The mono-substituted meta-diamines and the di-substituted meta-diamines containing one free para-position with respect to an amino-

group interact readily with diazonium salts to furnish para-aminoazo-colouring matters * (Trans., 1900, **77**, 1205; 1902, **81**, 89) and this reaction takes place with equal readiness both with the primary meta-diamines of this type and with their completely alkylated derivatives (Trans., 1902, **81**, 656).

2. The di-para-substituted primary meta-diamines



interact with diazonium salts to form ortho-aminoazo-derivatives, but the reaction takes place much less readily than with those diamines having one free para-position and the yield of azo-product is frequently very small (Trans., 1902, **81**, 88, 1379; 1905, **87**, 935).

3. The nature of the substituents X and Y exerts some influence on the course of the azo-condensation, for when they are methyl groups the base (4 : 6-diamino-*m*-xylene) reacts with diazotised aniline and its homologues, but when both substituents are halogen atoms (chlorine, bromine, or iodine) the condensation does not occur with these simple diazonium salts, but only with those derived from the nitroanilines. When only one methyl group is replaced by chlorine or bromine, reaction with diazotised aniline and *p*-toluidine still occurs, but the yield of *o*-aminoazo-derivative is extremely small (Trans., 1902, **81**, 1379; 1905, **87**, 937).

4. The presence of a nitro-group in one of the two substituted para-positions facilitates the azo-condensation, particularly when the diazonium salt also contains a substituent nitro-group (Trans., 1905, **87**, 940).

5. The progressive alkylation of the di-para-substituted meta-diamines rapidly reduces their capacity for forming azo-derivatives. The symmetrically and unsymmetrically dimethylated diamines give mixtures of diazoamines and aminoazo-compounds (Trans., 1905, **87**, 946; 1906, **89**, 1057, and this paper, p. 368), whilst the trimethylated diamines readily furnish diazo-amines and show scarcely any tendency to form azo-derivatives (p. 369). Finally, the interaction of the di-para-substituted *m*-diamines and diazonium salts is entirely prevented by the complete alkylation of these bases (Trans., 1902, **81**, 656).

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

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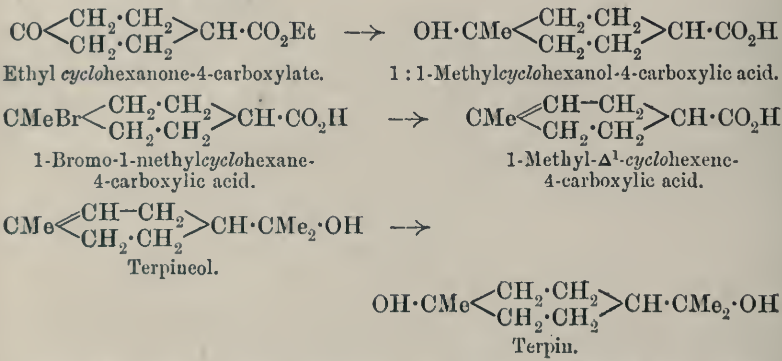
* Occasionally a small proportion of an ortho-aminoazo-derivative may appear as a by-product (Noelting and Thesmar, *Ber.*, 1902, **35**, 646).

XL.—*Experiments on the Synthesis of the Terpenes. Part I.* (*continued*). *Direct Synthesis of Terpin from Ethyl* cyclo*Hexanone-4-carboxylate.*

By FRANCIS WILLIAM KAY and WILLIAM HENRY PERKIN, jun.

IN Part I of these researches (Trans., 1904, **85**, 658) it was shown that ethyl 4-*cyclo*hexanone-1-carboxylate may be converted into terpin by the following steps:



$\mathrm{CO}\Big<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CO_2Et} \longrightarrow \mathrm{OH\cdot CMe}\Big<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CO_2H}$

Ethyl *cyclo*hexanone-4-carboxylate. 1 : 1-Methyl*cyclo*hexanol-4-carboxylic acid.

$\mathrm{CMeBr}\Big<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CO_2H} \longrightarrow \mathrm{CMe}\Big\ll\begin{array}{l}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CO_2H}$

1-Bromo-1-methyl*cyclo*hexane-4-carboxylic acid. 1-Methyl-Δ^1-*cyclo*hexene-4-carboxylic acid.

$\mathrm{CMe}\Big\ll\begin{array}{l}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CMe_2\cdot OH} \longrightarrow$

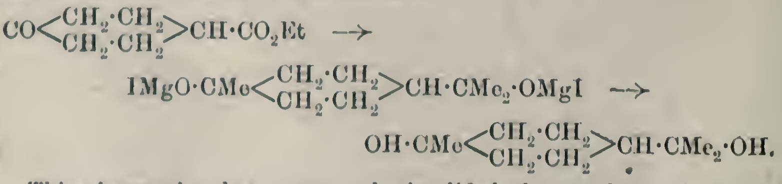
Terpineol.

$\mathrm{OH\cdot CMe}\Big<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CMe_2\cdot OH}$

Terpin.

The first step in this synthesis consists in treating ethyl *cyclo*hexanone-4-carboxylate with magnesium methyl iodide, and it was noticed that, after the product of the reaction had been decomposed by hydrochloric acid in the usual manner and the ethereal solution separated and evaporated, the weight of oil obtained was always considerably less than should theoretically have been produced.

In order to ascertain the reason of this discrepancy, a further series of experiments was instituted, and it was then discovered that the loss was due to the fact that a considerable amount of terpin remained in the aqueous solution after the ethereal layer had been separated. This direct formation of terpin from ethyl *cyclo*hexanone-4-carboxylate is easily understood, and is obviously due to the carbethoxy-group as well as to the keto-group of the ester reacting with the excess of magnesium methyl iodide always employed:



$$\mathrm{CO}\Big<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CO_2Et} \longrightarrow \mathrm{IMgO\cdot CMe}\Big<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CMe_2\cdot OMgI} \longrightarrow \mathrm{OH\cdot CMe}\Big<\begin{array}{l}\mathrm{CH_2\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}\end{array}\Big>\mathrm{CH\cdot CMe_2\cdot OH}.$$

This observation has very much simplified the synthesis of terpin, since it is now no longer necessary, in carrying out this synthesis, to pass through the several steps mentioned at the commencement of this paper.

The experimental details are as follows.

Ethyl *cyclo*hexanone-4-carboxylate (50 grams) is treated with magnesium methyl iodide (containing 12 grams of magnesium) in the usual manner (Trans., 1904, **85**, 660), and, after decomposing with dilute hydrochloric acid, the ethereal solution is separated and the aqueous solution saturated with ammonium sulphate and extracted, at least twenty times, with large quantities of ether on the shaking machine. The ethereal extract is dried over calcium chloride and evaporated, when a viscid, pale yellow syrup is obtained which gradually crystallises.

The mass is left in contact with porous porcelain until free from oil, and the residual, almost colourless, terpin boiled with water and animal charcoal and filtered, when *cis*-terpin gradually separates in glistening crystals melting at 117°. After remaining exposed to the air until dry, the following results were obtained on analysis:

0·1473 gave 0·3426 CO_2 and 0·1520 H_2O. C = 63·4; H = 11·5.
0·1620 ,, 0·3751 CO_2 ,, 0·1698 H_2O. C = 63·2; H = 11·6.

$C_{10}H_{20}O_2,H_2O$ requires C = 63·3; H = 11·6 per cent.

A careful comparison of this synthetical substance with ordinary *cis*-terpin hydrate proved conclusively that the two specimens were identical. The amount of terpin hydrate produced from 50 grams of ethyl *cyclo*hexanone-4-carboxylate under the above conditions varied in different experiments, but it was always considerable and in one case amounted to 7 grams. It is probable that this yield would be largely increased if a greater excess of magnesium methyl iodide were employed and the reaction allowed to proceed for several days.

THE SCHUNCK LABORATORY,
THE VICTORIA UNIVERSITY OF MANCHESTER.

XLI.—*The Rapid Electroanalytical Deposition and Separation of Metals. Part I. The Metals of the Silver and Copper Groups and Zinc.*

By HENRY JULIUS SALOMON SAND.

THE fact that the rate of electrolytic metal deposition can be greatly increased by rapid circulation of the electrolyte has been made use of in the employment of certain processes for many years. It appears that as early as 1886 a patent was taken out by Elmore for a method of depositing copper in which the electrolytic liquid was rapidly circulated, and several other processes based on the same principle have since been introduced.*

The effect of stirring the electrolyte during the simultaneous liberation of two constituents was demonstrated by the author in 1901 in a paper on the determination of concentrations in the layer of liquid touching the electrode. It was shown in the case of an acid solution of copper sulphate that convection currents play as great a part in the determination of the ratio of the two constituents liberated at the cathode as any of the other conditions of the experiment, and in one case in which less than 40 per cent. of the current was employed in depositing copper and more than 60 per cent. in generating hydrogen, the latter effect was suppressed altogether by simply stirring the electrolyte without altering the current (*Phil. Mag.*, 1901, [vi], 1, 45). It thus follows that the current-intensity which may be usefully employed in electrolytic metal deposition, and with it the duration of an experiment, depend entirely on the degree of stirring.

In 1903, vigorous stirring of the electrolyte for electroanalytical purposes was introduced in America almost simultaneously by Gooch and Medway (*Amer. J. Sci.*, 1903, [iv], **17**, 320, and **18**, 56) and Exner (*J. Amer. Chem. Soc.*, 1903, **25**, 896). The former rapidly rotated the cathode consisting of a platinum crucible, the latter, the anode formed of a wire spiral. The results were strikingly good in spite of the somewhat primitive methods of stirring employed, Exner in particular succeeded in reducing the time for a copper deposition to five minutes. Other forms of apparatus for rapid electroanalysis have been described by F. Mollwo Perkin (*Chem. News*, 1903, **88**, 102) and Smith and Kollock (*J. Amer. Chem. Soc.*, 1905, **27**, 1255); and of those who have published results on rapid electrodeposition, Amberg (*Zeitsch. Elektrochem.*, 1904, **10**, 383), Fischer and Boddaert (*ibid.*, 945), Smith and Kollock (*loc. cit.*), Davison (*J. Amer. Chem. Soc.*, 1905, **27**, 1275), Flora (*Amer. J. Sci.*, 1905, [iv], **20**, 268), R. O. Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 1287), Price and Judge (*Chem. News*, 1906, **94**, 18) may be mentioned.

All the methods used hitherto are, however, unsuitable for the purpose for which from its very nature electrolysis with rapid stirring specially lends itself, namely, for the separation of metals by graded potential.

Although this mode of analysis was first suggested by Kiliani in 1883 (*Berg u. Hüttenmännische Zeitung*), and more fully elaborated and theoretically justified by Freudenberg working in Ostwald's laboratory in 1893 (*Zeitsch. physikal. Chem.*, 1893, **12**, 97), yet so far as

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* For an account of methods of this kind, see Sherard Cowper-Coles, *Trans. Faraday Soc.*, 1905, **1**, 218.

I am aware it has not become known to analysts to any appreciable extent. As carried out by Freudenberg, the method of separating one metal from another consisted in regulating the voltage between the electrodes so that it should always remain below the value at which the second metal begins to deposit. The maximum electromotive force which thus becomes available at any time for impelling the current through the electrolyte is equal to the difference between the deposition potentials of the two metals in question, and generally amounts to a fraction of a volt. In order that fairly considerable currents such as must be employed for rapid electroanalysis may be used, it becomes a matter of paramount importance that the electrodes should be arranged so that the resistance offered by the liquid between them is as small as possible. In Exner's experiments the pressures between the electrodes attain to 19 volts, so that his apparatus is useless for the purpose in question, and the same must be said of the other methods hitherto described.

Freudenberg's separations depend on the assumption that the polarisation of the anode has a constant value, and this restricts them considerably. A much wider range will accrue to any method which allows the potential of the cathode alone to be conveniently measured by means of an auxiliary electrode. Such a method will also become practically independent of the resistance of the liquid, and will allow separations based on a very small difference of potential to be carried out.

Having had the opportunity of designing a set of electrodes for analysis, I therefore turned my attention especially to the following points of importance.

(1) Maximum stirring efficiency, which must be fairly independent of the quantity of liquid employed, so that it may be unnecessary to evaporate the latter after each washing.

(2) Very small resistance of the liquid, to be attained by bringing the electrodes as close together as possible.

(3) The possibility of conveniently using an auxiliary electrode to measure the potential of one of the electrodes.

(4) The possibility of washing the electrodes with a minimum amount of water.

*Apparatus.**—Figs. 1*a*, 1*b*, and 1*c* illustrate the apparatus designed to meet these requirements. It consists of a pair of platinum gauze electrodes, an inner rotating electrode, 1*c*, and an outer electrode, 1*a*, which surrounds it on all sides except the bottom. The two are kept in position relatively to each other by means of the glass tube 1*b*, which is slipped through the collar *A* and the ring *B* of the outer electrode. It is gripped firmly by the former, but passes loosely through the latter. The hollow platinum-iridium stem *A* of the inner electrode is passed through the glass tube, in which it rotates freely. The inner electrode is designed to produce a maximum amount of rotation of the liquid, and for this purpose has a vertical partition, *P*. It is open at the bottom and as open at the top as the requirement of rigidity in the construction of the frame will allow. The mesh of the gauze is 14^2 per sq. cm. The gauze of the outer electrode almost completely stops the rotation of the liquid. While the electrolyte is therefore ejected rapidly from the centre of the inner electrode by centrifugal force, it is continually replaced by liquid drawn in from the top and the bottom. So great is the suction thus produced that when the electrode is moving rapidly, chips of wood or paper placed on the surface are drawn down to the top of the outer electrode. The circulation is practically independent of the size of the beaker employed. As the outer electrode surrounds the inner completely, the lines of flow of the current are contained between the two, and even when strong currents are employed the potential of the electrolyte any-

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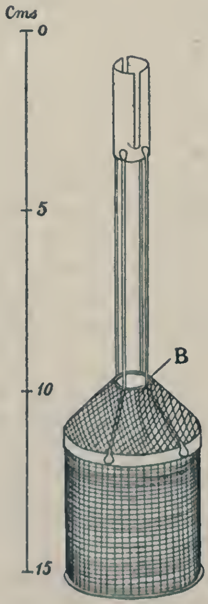
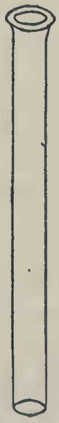
* The platinum apparatus was made by Messrs. Johnson and Matthey.

Fig. 1*a*. Fig. 1*b*. Fig. 1*c*.





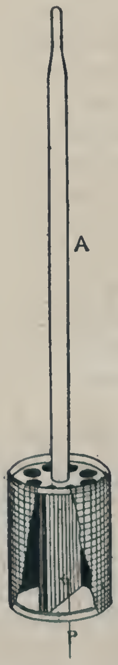


Fig. 1*a*.—Outer electrode. Fig. 1*b*.—Glass tube. Fig. 1*c*.—Inner electrode with part of gauze removed.

where outside the outer electrode is practically the same as that of the layer of liquid in immediate contact with it. This is a matter of great importance when an auxiliary electrode is employed, as it enables the potential difference electrode–electrolyte to be measured at any point in the liquid outside the outer electrode. The space between the surfaces of the two electrodes is about 3 mm. The weight of the outer electrode is about 40 grams, that of the inner electrode about 28 grams. Fig. 4 shows the stand. It will be seen that the beaker containing the electrolyte is always placed on a tripod support.

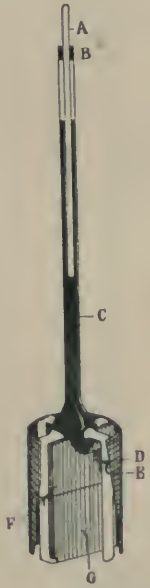


Fig. 2.—Inner electrode with glass frame. *A*, copper wire held in position in glass stem by slightly burnt rubber tube, *B*. *C*, mercury. *D*, piece of gauze fused through the glass, and, *E*, wire forming connexion between *C* and outer gauze. *G*, partition cut from microscope slide held in position by wire *F*.

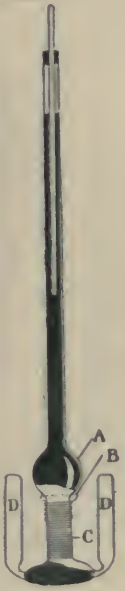


Fig. 3.—Inner electrode, No. 2. Stem and mercury as in Fig. 2. *A*, bulb to spread out gas bubbles. *B*, gauze fused into glass to make connexion. *C*, wire forming metal surface of electrode. *D*, *D*, vanes for stirring.

The outer electrode is gripped by a V-clamp, the cork from the flat side of which has been removed and replaced by platinum foil so as to obtain metallic contact. The inner electrode is held by a small chuck which is flexibly attached to the pulley from which the motion is derived. The figure will fully explain this, as well as the mode of electrical connexion by means of the mercury contained in the glass and rubber tubes *C* and *F*. There is thus practically no resistance in the rotating contact, and no chance of its being affected by the air of a chemical laboratory, a matter especially important when the potential difference of the two electrodes is measured for the purpose of separations. All movable connexions are made on the base of the stand on two sets of double terminals which are permanently joined to the holders of the electrodes by heavy flexible wire. Those parts of the stand which are exposed to the vapours from the electrolyte are painted with several coatings of a solution of celluloid in amyl acetate. In order to reduce the amount of platinum required for the apparatus, attempts were made to construct the frame of the inner electrode of

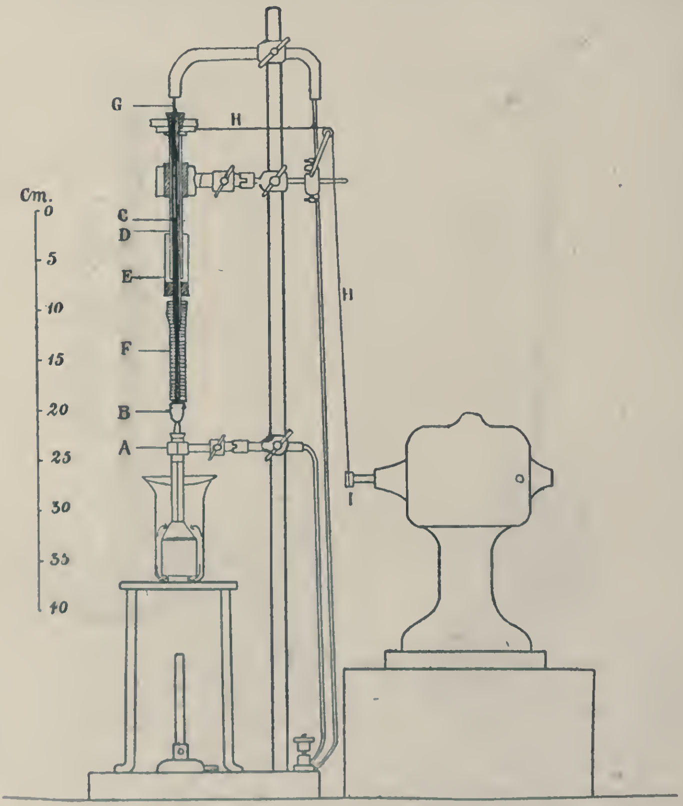


FIG. 4.—*A*, Clamp to grip outer electrode. *B*, Chuck to grip inner electrode. *C*, Glass tube rotating in glass tube *D*. *E*, Oil trap on *C*. *F*, Thick rubber tube. *G*, Amalgamated copper wire dipping into mercury contained in *C* and *F*. *H*, Cord made of violin string. *I*, Pulley made of rubber tube.

glass and at the same time to retain its essential features. Fig. 2 shows the result of these attempts. The electrode there depicted was in continual use for a month, after which the stem broke. The weight of platinum was less than 5 grams.

To avoid the use of platinum, it might perhaps be possible to make the outer electrode of silver when it is used as the cathode. It is probable that the metals deposited on it might be removed after electrolysis by the method of graded potential, although experiments in this direction have not yet been made.

As is explained later (p. 392), the electrodes 1*c* and 2 are not suitable for solutions containing metals which very readily pass from one stage of oxidation to another, such as copper in ammoniacal liquids, iron, tin, &c. In this case, an anode with a smaller oxidation and stirring efficiency is necessary. The former is obtained by making the surface of the electrode much smaller. Fig. 3 shows the electrode which was designed for this purpose. It is made almost entirely of glass, the total weight of platinum being 1½ grams.

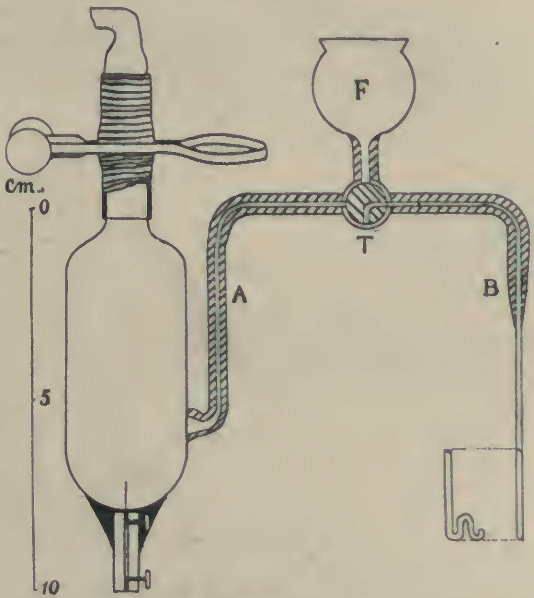


FIG. 5.

The Auxiliary Electrode.—The auxiliary electrode always used for the present investigation was a mercury-mercurous sulphate-2*N* sulphuric acid electrode. As an auxiliary electrode has hitherto not been employed in analysis, a special form (Fig. 5) suitable for this purpose was designed. The distinctive feature of this electrode lies in the funnel F and connecting glass tube $A\ B$. It will be seen that the two-way tap T will allow the funnel F to be connected with either half of the glass tube $A\ B$, or will close all parts from each other. The half A permanently contains the $2N$-sulphuric acid solution of the electrode. The half B, on the other hand, is filled for each experiment from the funnel F with a suitable connecting liquid, generally sodium sulphate solution. The end of B is made of thin tube of about 1½ mm. bore, and is bent round several times to minimise convection, as will be seen from the figure. While the electrode is in use, the tap, which must be kept free from grease, is kept closed, the film of liquid held round the barrel by capillary attraction making the electrical connexion, but towards the end of a determination a few drops are run out in order to expel any salt which may have diffused into the tube. The normal electrode is held in a separate stand so that it may easily be brought to or removed from the solution undergoing electrolysis.

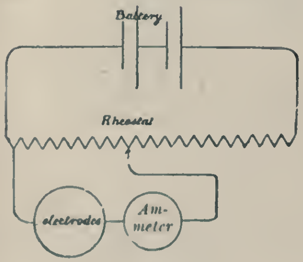


Fig. 6.

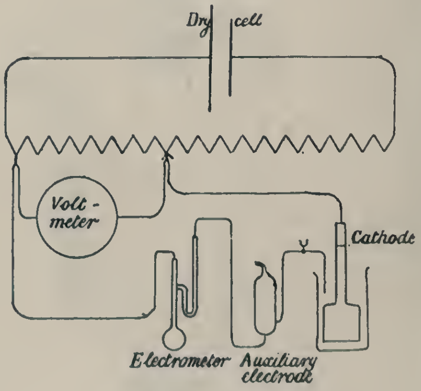


Fig. 7.

Electrical Connexions.—For separations by graded potential the electrical connexions must be made as shown in Fig. 6. The battery is connected directly to the two ends of a sliding rheostat, the electrolytic cell to one of them and the slider. It is manifestly essential that the sliding contact should be very good. A rheostat by Ruhstrat of Göttingen, with a carrying capacity of 15 amperes and a resistance of 2·6 ohms, proved very satisfactory. It was protected from the atmosphere of the laboratory by a coating of vaselin.

The arrangement (Fig. 7) adopted for the measurement of the potential difference auxiliary electrode-cathode is the one most usually employed at the present time in electrochemical research.

The electromotive force to be measured is balanced against a known electromotive force by means of a capillary electrometer. The known electromotive force is drawn from a sliding rheostat, the ends of which are connected with one or two dry cells. The value of the *E.M.F.* is read directly on a delicate voltmeter (range, 1·5 volts). For potential differences greater than 1·5 volts a Helmholtz 1 volt cell was interposed between the auxiliary electrode and the rheostat. The arrangement allows the voltage to be measured almost instantaneously, a matter of great importance in the present case. Owing to the very considerable advances that have been made in recent years in the construction of quadrant electrometers and their adjuncts, it seems probable that an electrometer might be permanently fitted up in such a manner as to be used as a direct-reading electrostatic voltmeter (range required, 1 volt; sensitiveness, 1 centivolt). If this were the case it would become as simple a matter to read the potential difference between the cathode and the electrolyte as that between the cathode and the anode.

Method of Carrying out an Experiment.—Where not specially stated to the contrary, the metal was always deposited on the outer electrode. To carry out an experiment the cathode, anode, and auxiliary electrode are placed in position, the electrolyte is heated to the required temperature and covered with a set of clock glasses having suitable openings for the electrodes. For the purpose of a separation the current is usually started at about 3—4 amperes and the potential of the auxiliary electrode noted. As a rule, this is only slightly above * the equilibrium potential. The current is then regulated so that the potential of the electrode may remain constant. When no by-reactions take place the current falls to a small residual value (generally about 0·2 ampere), as the metal to be separated disappears from the solution. The auxiliary electrode is then allowed to rise 0·1 to 0·2 volt, according to the metal.

It is obviously a matter of great importance to know when all the metal has been deposited. Under the conditions just assumed the amount deposited per unit of time may be taken as roughly proportional to the amount still in solution.[*] This being so, it follows that the amount in solution will decrease in geometrical ratio during successive equal intervals of time. If we therefore make the safe assumption that the concentration of the metal has fallen to under 1 per cent. of its original value in the time during which the potential and the current have been brought to their final value, it is clear that by continuing the experiment half as long again, the concentration of the metal will fall to under 0·1 per cent., so that the deposition can then be considered finished.

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* In the present paper the author proposes to adhere to the following nomenclature. The potential of an electrode or of an auxiliary electrode is said to be higher in one case than in another when it opposes the passage of the current to a greater extent in the first than in the second case, and this irrespective of any consideration whether the actual value becomes greater or smaller as a result of the arbitrary nature of the conceptions positive and negative electricity. When, however, numerical values are stated these are always given with their correct sign, and the following abbreviations have been employed. The potential of the cathode (or anode) is the difference of potential between it and the auxiliary ($2N$-sulphuric acid) electrode. The potential of the auxiliary electrode is the difference of potential between it and the electrode undergoing measurement. A great deal of confusion unfortunately exists in contemporary literature, especially with regard to the sign of potential differences, but the above nomenclature seems simple and rational.

In cases where by-reactions occur, the current does not fall to zero, but it generally attains a constant value which allows one to see when all the metal has been removed. In certain cases, the absence of the latter can be roughly tested for chemically, and by continuing the experiment for about half as long again as this reaction demands, the metal may be safely assumed to have been deposited completely. This method may be adopted, for example, in the separation of lead from cadmium, the former being roughly tested for by sulphuric acid. If none of these methods is available, the metal must be deposited to constant weight or else the separation must be carried out under very carefully defined conditions for a length of time proved more than sufficient by previous experiment.

Interrupting an Experiment.—A short time before completing the analysis, the inside of the tube 1_6, the sides of the beaker, and the clock glasses are washed by the aid of a wash-bottle and a few drops of liquid run out of the connecting limb of the auxiliary electrode. To interrupt the experiment, the auxiliary electrode and the clock glasses are removed, the tripod is then taken from under the beaker and the latter lowered until the surface of the liquid is just below the outer electrode. During this time the latter is washed. The stirrer is now stopped before lowering the beaker any further. The latter is then replaced by a slightly larger one, the tripod put back, and the electrode again washed. It is then disconnected, shaken, dipped first into a jar containing alcohol, shaken, then into another containing ether, and then dried for about half a minute over a Bunsen burner. The collar *A* is carefully dried by a silk cloth before weighing. The remaining liquid is washed into the larger beaker and is then ready for the deposition of the next metal.

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[*] This is based on the supposition that the concentration of metal in the layer of liquid touching the electrode is kept practically at zero during the whole of the experiment (see Brunner, *Zeitsch. physikal. Chem.*, 1903, **47**, 56). When this is not the case, the first stages of the separation are somewhat protracted, and if the duration of the whole experiment is made to conform with them, it therefore becomes a little longer than absolutely necessary, a matter which is, of course, of no importance for the result.

When only one metal is contained in the solution undergoing analysis, it is simpler to stop the stirrer, take away the beaker, and replace it by two successive ones containing distilled water. In both cases the current is left on during the process of interruption.

The beaker in which the first deposition of a separation is carried out was only slightly wider than the electrode and the amount of liquid roughly 85 c.c. In the second separation the amount was usually 130 c.c. and so on.

The rate of stirring varied very considerably from one experiment to another without greatly affecting the result. It may be taken as having been between the limits of 300 and 600 revolutions per minute.

Conditions for Obtaining Adherent Metal Deposits.

In electroanalytical experiments the question of obtaining firmly adherent deposits continually presents itself. This matter has been treated in several recent American papers (Bancroft, *J. Physical Chem.*, 1905, **9**, 277; Snowdon, *Trans. Amer. Electrochem. Soc.*, 1905, **7**, 143; Betts, *Trans. Amer. Electrochem. Soc.*, 1905, **8**, 63). A noteworthy discussion on the theory of the inclusion of metalloids and other phenomena occurring during metal deposition is also due to Jordis (*Zeitsch. Elektrochem.*, 1905, **11**, 787).

1. *Uniform Distribution of the Deposit over the Electrode.*—This is a matter which, apart from the shape of the electrode, depends solely on the relation between polarisation (in its broadest sense) and the electromotive force required according to Ohm's law to drive the current from one part of the liquid to another. It has been discussed by the author in some detail (*Zeitsch. Elektrochem.*, 1904, **10**, 452). The case of metals, such as cadmium and zinc, requiring a higher potential for their precipitation from the majority of their solutions than hydrogen should also be discussed here. These metals can only be deposited in virtue of the supertension, required to liberate the hydrogen as a gas. This supertension varies according to the material of the electrode, and even according to the state of its surface in various parts. It may therefore happen that the metal is deposited on a part of the electrode with a high supertension and continue to grow there, whilst at rougher parts of the electrode only hydrogen is evolved. Some solutions appear to be more sensitive to these variations in the quality of the electrode than others. Thus, in the case of zinc, a beautiful uniform deposit was once obtained from a boiling ammoniacal solution, but on repeating the experiment the precipitate obtained was patchy and useless.

2. *The Actual Nature of the Deposits.*—These may be classified as spongy, coarsely crystalline, and finely crystalline. Only the last-named are in general suitable for the purposes of the analyst.

Spongy deposits are probably in most cases due to the fact that the metal has been primarily produced in the form of an unstable compound, generally a hydride which has subsequently decomposed with the evolution of gas. A typical instance of this is afforded by bismuth. Depositions of this metal in an adherent form by slow methods have been described by Wimmenauer (*Zeitsch. anorg. Chem.*, 1901, **27**, 3); Brunck (*Ber.*, 1902, **35**, 1871); Kammerer (*J. Amer. Chem. Soc.*, 1903, **25**, 83). The real condition necessary for the production of a dense deposit was, however, understood by none of these experimenters. Consequently they give details of current strength, voltage, &c., which in their turn depend to a very great extent on the apparatus employed and on the amount of convection which may take place during the determination. It thus happened that Fischer and Boddaert (*loc. cit.*), working in the Aachen laboratory, failed to repeat their experiments. As will be seen from the present paper, bismuth can be obtained in an adherent form from nearly any solution, if only the potential of the cathode is kept low enough to prevent the formation of a hydride. If the potential of the electrode is not kept under control, the general conditions which keep it low and thus cause the production of a dense deposit are vigorous circulation of the electrolyte, small current density, and the presence of an oxidiser (nitric acid), and these conditions have been empirically employed to a greater or smaller extent by those investigators who have hitherto been successful in the deposition of bismuth. Copper behaves in a manner similar to bismuth, although in its case the phenomena are much less marked.

In certain cases, the precipitation of a metal hydroxide due to hydrolysis in consequence of the impoverishment of the solution in the layer of liquid adjacent to the electrode may also give the deposit a spongy appearance (see Bancroft, *loc. cit.*).

All the conditions discussed later, which may be considered to hasten the transformation of an unstable into a stable form, are also found to militate against the formation of spongy deposits.

The majority of electrolytic metal deposits are crystalline in structure, and may be either coarse- or fine-grained. The former are apt to lead to the formation of trees, from causes which must be classified under (1), and are usually loose; the latter are the deposits which are most desirable from the plater's point of view.

In considering the question of the fine-grainedness of a metal deposit, Bancroft (*loc. cit.*) has adopted a view originally put forward by Pfanhauser (*Galvanoplastik*, p. 73), that the crystallisation of electrolytic metal coatings is analogous to the crystallisation of salts from solution, and in the elaboration of this view he comes to the conclusion that a high current density and potential difference, a low temperature and the presence of colloids favour a fine-grained deposit. Some of these views have been experimentally verified by Snowdon.

With regard to these views the author of the present paper wishes to make the following additional remarks. The production of crystals is in almost all cases bound up with the intermediate formation of a metastable state. Thus crystallisation from a solution is probably always connected either with local supersaturation or with the intermediate production of an under-cooled liquid. In a similar way, it seems very probable that metal deposits are produced electrolytically in the first instance in a metastable state, and that it depends on the ease and rapidity with which this state is destroyed whether a fine- or a coarse-grained deposit is to be the ultimate result. This view comprises that recently put forward by E. Müller and Bahntje (*Zeitsch. Elektrochem.*, 1906, **12**, 317), that metals are deposited in the first instance in a colloidal state. The general conditions that would, on the author's view, favour a dense deposit are therefore the same as those put forward by Bancroft. Of these, experience shows that a high potential of the electrode is by far the most important. The reasons of analogy advanced by Bancroft for the favourable effect of a low temperature on the density of the deposit, however, appear to be inapplicable and not to be borne out by experience.

When colloids are present in the solution, these are often deposited with the metal (see Müller and Bahntje, *loc. cit.*) and effectually hinder crystallisation. The metal may thus be precipitated in a beautifully burnished condition. In the present investigation, copper was in one experiment obtained in a beautifully burnished state of the appearance of bronze by the electrolysis of a cold solution containing a large amount of ammonium acetate, the weight being about 2 per cent. too high. The explanation is probably to be sought in the presence of colloidal substances, either owing to accident or to the action of the current on the acetate.

EXPERIMENTAL.

Silver.—The precipitation of silver for analysis was studied in nitric acid, acetic acid, ammoniacal and potassium cyanide solutions. One of the difficulties encountered in nitric acid solutions consists in the formation of silver peroxide on the anode. Owing to the instability of this compound at higher temperatures, it is, therefore, possible to avoid its production by maintaining the solution at boiling temperature. The silver is then obtained as a uniform and coarsely crystalline, white deposit. It is, however, somewhat loose, and in consequence the results are not trustworthy when large quantities have to be precipitated. In separations of traces of silver from other metals the method could probably be employed with advantage. Several determinations were carried out in which more than half a gram of silver was deposited with an error of about 3 milligrams. The solutions contained between 1 and 2 c.c. of strong nitric acid per 85 c.c., and a current strength starting at 3 amperes and falling to 0·2 ampere was employed in such a manner that the auxiliary electrode showed a potential below 0·10 volt.

For the purpose of separations from other metals the method may in certain cases be improved by coating the cathode with mercury and thus obtaining the silver as an amalgam. This amalgam is adherent only when in a semi-liquid state, and in consequence it is necessary to employ at least ten times as much mercury as silver. The experiments were carried out with the potential of the cathode regulated to a minimum as if a separation from other metals were being effected. For reasons explained later (p. 389), it is therefore essential to keep the solution at the boiling point. Tartaric acid was added, as this reagent is required in some of the separations. The method of drying the electrode was the same as that used for mercury (see later). The following result was obtained under these conditions.

Experiment.—The electrode was coated with about 1·5 grams of mercury. The solution contained 0·2332 gram of mercury as nitrate, 18 grams of tartaric acid, and 1 c.c. of concentrated nitric acid per 85 c.c. During electrolysis it was observed to become turbid and finally clear.

Ag taken.	Ag found.	Amps.	Volts, auxiliary.	Temp.	Time in minutes.
0·1078	0·1072	7—0·2	0—0·15	boiling	7

As silver is deposited from acetic acid solutions containing a large amount of acetates at a higher potential than from nitrate solutions (in consequence of the small number of Ag ions present), it was to be expected according to the general considerations advanced above that a more finely crystalline, and therefore firmer, precipitate would be obtained. This proved to be the case, the silver deposit remaining unaltered by tapping, and almost so by scraping with a horn spatula. In consequence, the results obtained were sufficiently good to make the method suitable for analysis. The following experiments were carried out.

Experiments.—In Nos. 1, 2, 3, and 5, silver was deposited on the electrode, weighed, and dissolved in a solution of 5 c.c. of concentrated nitric acid; 25 grams of ammonium acetate were then added and the solution was heated to boiling, the burner being removed during deposition. In experiment 4 the electrolyte contained a known quantity of silver nitrate solution analysed according to the ammonia method (see later), to which 5 c.c. of concentrated nitric acid and 20 grams of ammonium acetate were added

No.	Ag taken.	Ag found.	Amps.	Volts between anode and cathode.	Temp.	Time in minutes.
1.	0·5373	0·5365	3·5—0·2	1 —1·3	boiling	8
2.	0·5363	0·5361	3·5—0·2	1 —1·3	,,	8
3.	0·5361	0·5358	4 —0·2	1 —1·3	,,	7
4.	0·5389	0·5397	3 —0·2	1 —1·2	,,	6
5.	0·5397	0·5399	5 —0·2	1·1—1·2	,,	6

As silver is deposited from ammoniacal solutions at a higher potential than from acetate solutions, it was expected that a still firmer deposit would be obtained, and this proved to be the case. The deposits were unattacked by both tapping and scraping. The solutions were kept boiling vigorously during deposition. As there are practically no sources of error apparent in this method, the results obtained by it are probably always exceedingly trustworthy. The following experiments were carried out.

Experiments 1, 2, 3.—The silver was deposited on the cathode, weighed, and dissolved in acid containing 10 c.c. of concentrated nitric acid. Fifteen c.c. of concentrated ammonium hydroxide were then added :

No.	Ag taken.	Ag found.	Amps.	Volts between anode and cathode.	Temp.	Time in minutes.
1.	0·5371	0·5371	3—0·2	1—1·3	boiling	8
2.	0·5371	0·5373	5—0·2	1—1·3	,,	7
3.	0·5354	0·5352	4—0·2	1—1·3	,,	7

Silver is precipitated from alkaline cyanide solutions at a much higher potential than from the foregoing, and accordingly leaves nothing to be desired as regards density of the deposit. Nevertheless, there are undoubtedly more sources of error in this method than in the others, as alkaline solutions containing organic substances appear to cause difficulties due to the decomposition products formed at the anode (see p. 401). Exner (*loc. cit.*) obtained correct results for silver from cyanide solutions, but Fischer and Boddaert (*loc. cit.*) consistently obtained numbers about 0·5 milligram low. The following are the results obtained in the present investigation.

Experiments.—In No. 1 metallic silver was deposited on the electrode, weighed, and dissolved in an acid solution containing 3 c.c. of concentrated nitric acid; the latter was neutralised with ammonia and about 2·5 grams of potassium cyanide were added, the temperature being about 90°. Experiment 2 was as 1, but the quantities were 15 c.c. of concentrated nitric acid, neutralised by ammonia and 4 grams of potassium cyanide. In experiment 3 a measured volume of silver solution was used together with 5 c.c. of concentrated nitric acid, 3⅓ grams of sodium hydroxide, and 3 grams of potassium cyanide:

No.	Ag taken.	Ag found.	Amps.	Volts * anode–cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·5389	0·5361	8—5	3·5	—	90°	6
2.	0·5361	0·5340	10—9	3·8—3·9	—	90	6
3.	0·2694	0·2699	3—0·2	—	1·15—1·25	60	9

* Rough values.

Mercury and its Separation from Silver.

One of the chief differences from the analyst's point of view between the electrolytic determination of mercury and that of other metals lies in the manner of drying which must be adopted in consequence of the volatility of this metal. The method usually recommended consists in placing the wet electrode in a vacuum desiccator. As it was realised that a great part of the advantage resulting from rapid deposition is lost if a lengthy drying process is employed, several experiments were carried out with the object of shortening this operation. A current of dry air was drawn over the electrodes; the latter, however, always lost weight. Air saturated with mercury vapour was then tried both hot and cold. In the former case the electrode gained in weight, in the latter it remained constant. Thus 0·6241 gram of mercury was deposited on the cathode, dried, weighed, then dipped into water, allowed to drain on filter paper for a few minutes, and dried for an hour and a half according to the above method. The weight found was 0·6242 gram. The apparatus employed is shown in the accompanying Fig. 8, and will need no further explanation. The time varied in different experiments between forty minutes and two hours. The electrode was always dried until constant in weight.

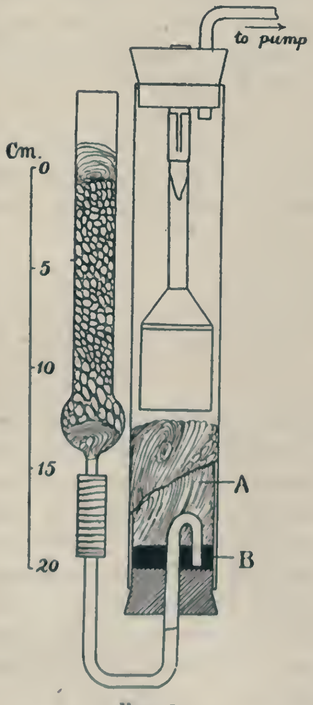


FIG. 8.
A. Cotton wool.
B. Mercury.

It is well known that mercury may be deposited from nitrate solutions either in loose drops unsuited for weighing or as a mirror, but so far as I am aware it has never been pointed out that the former always occur at first during deposition while the potential of the cathode is low, and it is only when the potential rises and hydrogen is given off that the mercury spreads out as a mirror.

From ammoniacal and cyanide solutions the mercury is precipitated in exceedingly fine drops which adhere to the electrode sufficiently for their quantitative estimation.

When nitrate solutions are employed in quantitative separations by graded potential from metals such as copper and bismuth, it is manifestly impossible to allow the potential of the cathode to rise to the value at which a bright mirror is formed. In order to obtain deposits sufficiently adherent for quantitative purposes, it is in this case essential to keep the solution boiling during deposition. In Exner's experiments the solution was maintained at a temperature slightly below 100°. Fischer and Boddaert, however, obtained too low results working according to this method, and state that it is necessary to keep the electrolyte at the ordinary temperature. Owing to the very appreciable volatility of mercury at high temperatures, there must always be considerable risk of loss if hydrogen is generated rapidly on the surface of the electrode in a hot solution. In separations by graded potential in which there is no possibility of the production of hydrogen, this objection to high temperatures obviously does not hold. In all cases, great care was taken to keep the surface of the mercury covered completely by the electrolyte.

The amount of mercury which may be precipitated on the gauze electrode is very considerable, 2 to 3 grams having been deposited in a form sufficiently adherent to prevent any possibility of loss by vigorous shaking. For the purpose of weighing, the electrode was suspended to the balance by a wire. An objection to the use of the gauze electrode should be stated here. It is the very considerable loss in weight which the gauze undergoes when the mercury is removed. It amounted, as a rule, to about 3 milligrams. This objection would be largely overcome if it were possible to obtain gauze commercially made of platinum-iridium instead of platinum wire. The following determinations were carried out:

Experiments 1 *and* 2.—A weighed quantity of mercury was dissolved in nitric acid, evaporated to dryness on the water-bath, nitric acid added and made up to a known volume. Of this solution measured quantities were taken. The amount of free nitric acid present in the solution amounted to about 1½ c.c. per 85 c.c.:

No.	Hg taken.	Hg found.	Amps.	Volts anode–cathode.	Temp.	Time in minutes.
1.	0·5830	0·5833	9	2·6—3·7	warm	5
2.	0·5830	0·5831	9	—	,,	5

Experiment 3.—Ammonia method with limited potential; 10 c.c. of concentrated nitric acid and 20 c.c. of concentrated ammonium hydroxide were added to the solution, which was heated nearly to boiling during electrolysis:

Hg taken.	Hg found.	Amps.	Volts auxiliary.	Time in minutes.
0·4665	0·4672	3—0·2	0·40—0·50	6

Separation from Silver.—As mercury is deposited from most solutions at almost the same potential as silver, it seems hopeless to effect a separation by graded potential. In the books on electro-analysis it is stated that the two may be deposited together and the mercury expelled by ignition. Details are, however, not given. As a temperature above the melting point of silver is said to be necessary for the complete decomposition of silver-amalgam (Gay-Lussac, see Dammer, *Handb. Anorg. Chem.*, 2, 943), it was thought undesirable, to endanger the electrode by experiments in this direction. The metals were therefore deposited together, dissolved in nitric acid, and separated by the cyanide method. The pure silver cyanide thus obtained was dissolved in potassium cyanide and analysed by electrolysis. An experiment in which the combined nitrates of silver and mercury were evaporated to dryness and ignited strongly in a porcelain crucible in the hope that only pure silver might be left behind, failed owing to the formation of a mercury compound with the glaze of the crucible.

Experiment.—The cathode was plated with about 1·5 grams of mercury (see p. 386), weighed, and the mercury and silver deposited into this from a boiling solution containing 1 c.c. of concentrated nitric acid and 18 grams of tartaric acid (the latter was added as it was thought that its presence might probably be required in later separations from other metals). After weighing, the combined metals were dissolved in a boiling solution containing 20 c.c. of concentrated nitric acid; the liquid was then made alkaline with sodium hydroxide faintly acid with nitric acid and potassium cyanide added to it until it was clear. It was then warmed slightly and the silver precipitated by nitric acid, allowed to settle and collected. The filter paper with the silver cyanide was then added to a solution containing about 3·5 grams of potassium cyanide, and the silver deposited at about 80° with a current of 3 amperes; the stirrer was kept moving slowly to prevent too great disintegration of the paper.

Hg + Ag taken.	Hg + Ag found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
0·4488	0·4486	5—0·2	0—0·10	boiling	14

Ag taken = 0·2156 Ag found = 0·2132

Copper and its Separation from the preceding Metals.

No difficulty was experienced in depositing copper from nitrate and sulphate solutions. As is known, a smooth deposit is obtained from nitric acid solutions, whereas the copper produced in solutions containing only sulphuric acid is usually slightly powdery at the end of the experiment. This is no doubt due to the intermediate formation of a copper hydride, when the potential rises to the value at which hydrogen is evolved. In solutions containing nitric acid or other oxidising agents this cannot take place, as reduction first sets in. Even from sulphuric acid solutions smooth deposits may be obtained if the metal is deposited at a limited potential of the cathode. A slightly powdery surface of the deposited copper does not appear to cause loss in washing, and thus does not affect the accuracy of the results. The loss in washing in solutions containing free nitric acid also appears to be negligible, so long as oxides of nitrogen are absent. When, however, these were present even in traces after the solution of metallic copper in nitric acid, it was found necessary to add an alkali acetate to the solution before disconnecting. The following results were obtained:

Experiments.—Metallic copper was deposited on the electrode from an acid sulphate solution, weighed, dissolved in a solution containing 2·0 to 2·5 c.c. of concentrated nitric acid, redeposited, and 5 grams of sodium acetate (No. 1) or 7 grams of ammonium acetate (Nos. 2 and 3) added before disconnecting:

No.	Cu taken.	Cu found.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
1.	0·2939	0·2938	10	2·5	warm	6
2.	0·2504	0·2506	10	2·8	,,	6
3.	0·2504	0·2505	10	2·6	,,	6

For the following experiments, either measured quantities of a copper sulphate solution or weighed quantities of copper sulphate crystals (Kahlbaum) were taken, the amount of copper in both having been previously estimated according to the method proved correct by Nos. 1, 2, 3. In Nos. 4 and 5, 1 c.c. of concentrated nitric acid, in No. 6, 1 c.c. of concentrated sulphuric acid, in Nos. 7, 8, and 9, 0·75 c.c. of concentrated sulphuric acid were added. In No. 9 the free mineral acid was removed by ammonium acetate before disconnecting:

No.	Cu taken.	Cu found.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
4.	0·2474	0·2471	10	2·8	lukewarm	6
5.	0·2243	0·2239	10	—	hot	6
6.	0·2474	0·2476	10	3·0	lukewarm	6
7.	0·2949	0·2953	10—7	2·9—3	boiling	5
8.	0·2690	0·2693	10	2·8—3·2	hot	5
9.	0·2520	0·2517	10	2·8	boiling	7

As far as can be judged from the experiments carried out, the electrolysis of copper solutions containing free acetic acid and a considerable quantity of alkali acetates does not give accurate results. In some cases, values $1\frac{1}{2}$—2 per cent. too high (5 milligrams) were obtained. In other cases (see experiments on separation from silver) the results were better.

From boiling tartrate solutions, correct results for copper have been repeatedly obtained at limited potential. The copper is all deposited at a potential of the $2N$-sulphuric acid electrode below 0·60 volt.

Experiment.—$2\frac{1}{2}$ c.c. of concentrated nitric acid, 10 grams of sodium tartrate, volume 120 c.c.:

Cu taken.	Cu found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
0·2941	0·2927	3—0·2	0·45—0·55	100°	10

A difficulty arose in the experiments in ammoniacal solutions from the ready transformation of cuprous to cupric compounds and *vice versâ*, the anode effecting the former, the cathode the latter reaction. In consequence, the potential of the cathode does not rise high enough to allow all the copper to be deposited. Similar difficulties are met with frequently in electrolysis in the case of such metals as iron and tin, and to a very much smaller extent in the case of mercury. There appear to be three different principles by the application of which the difficulty may be met: (1) by the use of a diaphragm; (2) by the addition of reducing agents which may be oxidised at the anode in place of the whole or part of the salt undergoing electrolysis; (3) by lowering the oxidising and stirring efficiency of the anode. This can be done by making use of the anode depicted in Fig. 3 on p. 377.

The first method would be the most efficient, and would undoubtedly, if it were found possible to carry it out in a practicable manner, eliminate most of the difficulties which are still met with in electroanalysis.

The second principle comes into operation where solutions of oxalates, &c., are employed.

The third was found sufficient in the present case. The following experiments were carried out:

Experiments.—In Nos. 1 and 2 the following were added to the electrolyte, 1 gram of ammonium nitrate, 20 c.c. of concentrated ammonia solution; in No. 3, 10 c.c. of concentrated nitric acid and 17 c.c. of concentrated ammonia solution. The copper deposit was slightly discoloured:

No.	Cu taken.	Cu found.	Amps.	Volts anode-cathode.*	Temp.*	Time in minutes.
1.	0·2941	0·2937	3—5	4·5	20—50°	9
2.	0·2941	0·2937	3—5	4·5	20—50	10
3.	0·3682	0·3682	--	—	80	20

* Rough values.

Separation from Silver and Mercury.—Both silver and mercury can be deposited completely from nitrate solutions at a potential of the $2N$ sulphuric acid electrode below 0·10 to 0·15 volt, and as copper does not begin to be precipitated below 0·30 volt a separation can be readily effected. (For the conditions governing the adherence of deposits, see pp. 385, 389.)

Experiments 1 *and* 2.—About 0·75 c.c. of concentrated nitric acid per 85 c.c. :

No.	Taken.	Found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·5330 Hg	0·5850 Hg	10—0·2	0·0—0·15	boiling	6
	0·2465 Cu	0·2467 Cu	9	—	warm	5
2.	0·5830 Hg	0·5846 Hg	10—0·2	0·0—0·15	boiling	6
	0·2465 Cu	0·2469 Cu	—	—	—	—

Silver was separated from copper in boiling acetate solutions, both by the aid of an auxiliary electrode, the potential of the latter being kept less than 0·30 volt, and also by simply regulating the potential difference between the anode and the cathode below 1·25 volts. Before disconnecting, care must be taken to reduce the voltage sufficiently to preclude its rising above the fixed value during the operation.

Experiments.—In Nos. 1 and 2, the solution contained 5 c.c. of concentrated nitric acid and 25 grams of ammonium acetate ; in No. 3, 4 c.c. of concentrated sulphuric acid and 25 grams of sodium acetate ; in No. 4, 4 c.c. of concentrated nitric acid and 25 grams of sodium acetate. In experiment 4, 6 to 7 c.c. of concentrated nitric acid were added before depositing the copper :

No.	Taken.	Found.	Amps.	Volts anode-cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·5389 Ag	0·5394 Ag	2·5—0·4	1·0—1·25	—	boiling	9
	0·155 Cu	—	—	—	—	—	—
2.	0·5389 Ag	0·5386 Ag	2·8—0·5	1·0—1·20	—	boiling	7
	0·0990 Cu	0·0994 Cu	4	3	—	hot	4
3.	0·5389 Ag	0·5389 Ag	2·8—0·8	1·0—1·20	—	boiling	7
	0·2474 Cu	0·2483 Cu	6—3	2·6	—	hot	5
4.	0·2695 Ag	0·2705 Ag	2·7—0·4	—	0·30	boiling	—
	0·5882 Cu	0·5908 Cu	10	3·5	—	tepid	—

Silver may also be separated from copper in ammoniacal solutions with the aid of the auxiliary electrode if the potential of the latter be kept below 0·50 volt. As will be clear from the remarks on p. 392, the anode, Fig. 3, must be employed. It will also be understood that after complete deposition of the silver the current does not fall to zero. The absence of the latter must therefore be confirmed by means of hydrochloric acid.

Experiments.—10 c.c. of concentrated nitric acid, 15 c.c. of concentrated ammonium hydroxide solution :

No.	Taken.	Found.	Amps.	Volts anode-cathode.*	Volts auxiliary.	Temp.	Time in minutes.
1.	0·2170 Ag	0·2163 Ag	3—1·3	2	0·38—0·50	boiling	10
	0·3682 Cu	0·3680 Cu	4	5·4	—	warm	10
2.	0·2170 Ag	0·2165 Ag	5—1·5	3·5	0·45—0·50	boiling	9
	0·3682 Cu	—	—	—	—	—	—

* Rough values.

Bismuth and its Separation from all the preceding Metals.—As has already been pointed out, the precipitation of bismuth as such in a coherent form suitable for analysis has hitherto been considered one of the most difficult electroanalytical operations, and a satisfactory method can hardly be said to have been available.

In the present investigation, satisfactory results were obtained in acetate, tartrate, and nitrate solutions; the only condition which had to be observed was to keep the potential of the electrode as low as possible. A temperature of about 60° was found the most suitable. In solutions containing free nitric acid, the potential of the cathode is automatically kept low owing to the reduction of the acid if only the stirring efficiency is sufficient to prevent its local exhaustion. With the present electrodes it was found possible to use currents of 2 to 3 amperes without any further precaution, in contradistinction to the results obtained with different apparatus by other investigators. When tartrate and acetate solutions were employed, it was found necessary to keep the potential of the cathode carefully under control by means of the auxiliary electrode as described on p. 381. The following experiments were carried out:

Experiments 1 *and* 2.—Bismuth was deposited on the electrode from a nitrate solution, weighed, dissolved in an acid solution containing 2½ c.c. of concentrated nitric acid, then 8 grams of sodium tartrate were added. At the end of the experiment, before disconnecting the solution was made alkaline with 5 c.c. of concentrated ammonium hydroxide:

No.	Bi taken.	Bi found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·2184	0·2187	3—0·2	0·63—0·9	warm	9
2.	0·2999	0·2996	3—0·2	0·63—0·9	,,	9

A solution was then made up by dissolving approximately 14 grams of bismuth oxide (Kahlbaum) in a litre of acid containing approximately 100 c.c. of concentrated nitric acid. This solution was analysed according to the method proved correct by experiments 1 and 2 (two determinations, difference 0·3 milligram). Measured quantities of this solution were taken for the following experiments with the exception of Nos. 8, 11, and 12. In experiments 3—6, the solution contained about 2½ c.c. of concentrated nitric acid in 85 c.c.; the same electrolyte was employed in experiment 7, but neutralised with ammonia before disconnecting. In experiment 8, electrolytically deposited bismuth was dissolved in 2½ c.c. of concentrated nitric acid, then 10 grams of ammonium acetate added, and the cathode potential kept under control. In experiment 9, the electrolyte contained 10 c.c. of formaldehyde, but was otherwise identical with that of No. 7. In experiments 10—13, 2½ grams of concentrated nitric acid and 8 grams of sodium tartrate were present, and the solution was neutralised with sodium hydroxide before disconnecting; metallic bismuth formed the starting point in Nos. 11 and 12. In experiment 14, the solution contained 2½ grams of concentrated nitric acid and 12 grams of sodium tartrate:

No.	Bi taken.	Bi found.	Amps.	Volts anode–cathode.	Volts auxiliary.	Temp.	Time in mins.
3.	0·3223	0·3207	3—2	2·4	—	cold	8
4.	0·3223	0·3215	3	2·1—2·9	—	,,	11
5.	0·3223	0·3208	3	—	—	,,	11
6.	0·3223	0·3212	3	—	—	,,	12
7.	0·3223	0·3226	3—2	2·1—3·0	—	,,	9
8.	0·3207	0·3199	3·5—0·4	2·7	0·65—0·80	tepid	11
9.	0·3203	0·3198	4—0·2	—	0·65—0·80	,,	10
10.	0·3223	0·3216	2—0·2	2·4—1·9	0·65—0·90	cold	15
11.	0·3216	0·3203	2—0·2	—	0·65—0·90	,,	13
12.	0·3198	0·3194	2—0·2	—	0·65—0·90	,,	—
13.	0·2395	0·2389	3—0·2	—	0·63—0·75	hot	—
14.	0·3886	0·3882	3—0·2	1·3	0·65—0·70	boiling	11

Several determinations of bismuth as amalgam were also carried out, error 0·7—0·8 milligram on 0·2 gram of bismuth. The method requires far more time and trouble than the direct estimation and is probably less accurate than that of experiments 1 and 2.

Separation from the preceding Metals.—In the electropotential series for acid solutions, bismuth stands about 0·1 to 0·2 volt higher than copper, and can therefore be separated from silver and mercury in acid solution by the same methods as the former metal. Its separation from copper is, however, somewhat difficult in consequence of its close proximity to this metal. In nitric acid solutions the difference between the deposition potentials of the two metals is only about 0·10 volt, and a separation is quite impracticable. In boiling tartrate solutions containing free tartaric acid, copper is deposited at a potential between 0·40 and 0·60 volt and bismuth between 0·60 and 0·70 volt. As a result it is found that a separation by graded potential may be effected if the quantity of bismuth is very small by maintaining the potential of the auxiliary electrode below 0·60 volt. When, however, the quantity of bismuth is large, some of it is deposited with the copper, and must be separated from it by dissolving the metal in nitric acid and repeating the operation.

Experiments.—The solutions contained about 2½ c.c. of concentrated nitric acid and 10 grams of sodium tartrate. The copper depositions were repeated, the auxiliary electrode being maintained at 0·60 volt for two minutes in each. The numbers in brackets are the results of the first deposition :

No.	Taken.	Found.	Amps.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·2941 Cu	0·2929 (0·3033)	4—0·1	0·50—0·60	boiling	8
	0·3223 Bi	0·3221 Bi	4—0·2	0·60—0·80	hot	6
2.	0·2941 Cu	0·2926 (0·2993)	5—0·2	0·50—0·60	boiling	9
	0·3223 Bi	—	—	—	—	—

Another method of separating copper from bismuth has been suggested by E. Smith (*Amer. Chem. J.*, 1890, **12**, 428). It consists in preparing an alkaline solution of the two metals and adding potassium cyanide, thus converting the copper into a double cyanide, a compound which requires a very high potential for its decomposition. The bismuth does not form a cyanide, and can be deposited at a much lower potential. Smith recommends the use of a current of 0·2 ampere, and required nine hours for a separation.

Methods of separation with a fixed current strength, being devoid of a scientific basis, can, however, not be considered trustworthy. Satisfactory results may, on the other hand, be obtained by keeping the potential of the cathode under control. In the present case, the auxiliary electrode was kept below 1·40 volts. It was found necessary to use a hot solution and to prevent the formation of a deposit of bismuth pentoxide on the anode by the addition of formaldehyde. The bismuth was kept in solution by means of an alkali tartrate.

Experiments.—Copper and bismuth were deposited in weighed quantities on the cathode and dissolved in a boiling solution of 3 c.c. of concentrated nitric acid. Then 8 grams of sodium tartrate, 3 grams of sodium hydroxide, 5 grams of potassium cyanide, and 10 c.c. of formaldehyde were added. The current was kept low enough to prevent the blue colour of the alkaline copper tartrate from making its appearance (due to the decomposition of the potassium cyanide). The bismuth was taken to constant weight :

No.	Taken.	Found.	Amps.	Volts anode-cathode.*	Volts auxiliary.	Temp.	Time in minutes.
1.	0·3886 Bi	0·3871 Bi	2—0·2	0·4	1·08—1·40	roughly 80°	36
	0·2995 Cu	0·2990 Cu	10	3·5	—	boiling	8
2.	0·2503 Bi	0·2498 Bi	1·5—0·2	0·5	1·10—1·40	roughly 80°	23
	0·3590	0·3585	10	3·6	—	boiling	9

* Rough values.

Lead and its Separation from all the preceding Metals.—Lead may be determined both in the form of peroxide and as metal. In the form of peroxide its adherence to the electrode was found to depend greatly on temperature. In the cold it is very loose, and only small currents may be employed. When deposited from a boiling solution it is, however, exceedingly adherent, as has already been found by Exner, but a considerable strength of current must be used to counteract the solvent action of the acid. In the present investigation, it was deposited both on the inner and on the outer electrode. In the former case it was found desirable not to use very large quantities. The temperature chosen was about 60°.

Experiments.—A weighed quantity of pure lead (Kahlbaum) was dissolved in nitric acid, boiled to expel nitrous fumes, and made up to a known volume.

In experiment 1 the electrolyte contained 10 c.c. of concentrated nitric acid; in experiments 2—5, 15 c.c. of concentrated nitric acid per 85 c.c. The peroxide was deposited on the outer electrode in Nos. 1—3, on the inner electrode in Nos. 4 and 5. It was dried in the usual way at 200°:

No.	Pb taken.	Pb found as PbO_2.	Amps.	Volts anode–cathode.	Temp.	Time in minutes.
1.	0·1383	0·1374	3	2·4	roughly 60°	7
2.	0·3457	0·3465	3	2·2	,,	9
3.	0·3457	0·3455	3	2·2	,,	9
4.	0·1383	0·1365	2	2	,,	9
5.	0·1383	0·1384	2	2	,,	10

Lead may also be deposited as metal either in a faintly acid, an ammoniacal, or an alkaline solution, when reducing agents are added to prevent the formation of the peroxide. The reducing agent employed was either tartaric acid or glucose, and the solution was kept hot (see the experiments on the separation of lead from bismuth and from cadmium, pp. 399 and 402). The deposit is roughly crystalline and not very firm when obtained from an acid solution. It is denser when produced in an ammoniacal and still denser in an alkaline solution, corresponding to the potential of the electrode at which it is formed (see general considerations, p. 385).

Separation from the preceding Metals.—The separation of lead from other metals based on the fact that it can be deposited on the anode as peroxide is well known; the present electrodes, however, allow simplifications and improvements to be made in some cases. When it is desired to separate lead from a metal such as copper, there is no need to acidify the solution strongly with nitric acid in order to prevent the deposition of metallic lead if only the quantity of the copper is so great that all the lead is deposited on the anode a considerable time before exhaustion of the copper sets in. Thus an experiment was successfully carried out in which lead and copper were deposited in one operation from a solution containing sulphuric and nitric acids. A precipitate of lead sulphate was present, which, however, dissolved as the lead was deposited on the anode. It should be mentioned here that in certain other experiments attempts were made to separate metals from solutions containing precipitates which were not dissolved during the electrolytic operation. In nearly all such cases it was not found possible to wash the deposited metal free from the precipitate.

Experiment.—Measured quantities of the standardised copper sulphate and lead nitrate solutions were taken and 1 c.c. of concentrated nitric acid added. The solution was hot. A current of 2 amperes was passed for five minutes, during which all the lead sulphate disappeared and the liquid still remained blue. The current was then increased to 10 amperes and all the copper deposited. The inner electrode was the anode. The lead peroxide was not very adherent, but none was lost in washing:

Cu taken 0·2474; Cu found 0·2476.
Pb ,, 0·1383; Pb ,, 0·1386.

According to B. Neumann (*Analytische Elektrolyse der Metalle*, p. 176), the separation of lead as peroxide from silver is not trustworthy as the deposit is said frequently to contain small quantities of silver. Owing to the great instability of silver peroxide at 100° it was expected that if the solution were kept boiling during the deposition a quantitative separation could be effected, and this proved to be the case. The solutions employed were strongly acid. A small amount of silver was always precipitated in a very loose form on the cathode. This must be dissolved carefully in the nitric acid by heating the solution before it is made ammoniacal for the deposition of the silver.

Experiments.—The solutions contained 10 c.c. of concentrated nitric acid during the deposition of the lead. In No. 2, 5 c.c. more were added after the lead had been removed, to ensure the solution of all the silver, then the electrolyte was made strongly ammoniacal and the silver deposited. The lead peroxide was precipitated on the outer, the silver, after the removal of the latter, on the inner electrode:

No.	Taken.	Found.	Amps.	Volts anode-cathode.	Temp.	Time in minutes.
1.	0·2848 Pb	0·2857 Pb	3—4	1·6	boiling	10
	0·2694 Ag	—	—	—	—	—
2.	0·2848 Pb	0·2854 Pb	3	1·7	boiling	10
	0·2694 Ag	0·2693 Ag	3	—	,,	—

When lead peroxide is deposited from solutions containing salts of bismuth, it is known always to contain some of this metal and a purely electrolytical method of separation of lead from bismuth has hitherto not been available. It was expected that a separation might be effected by regulating the potential of the anode. This, however, proved not to be the case. In an experiment carried out with 0·15 gram of lead per 85 c.c. it was found that all the peroxide could be deposited at an anode-potential of 1·10 volts, the initial current being 3 amperes.

When, however, about 0·4 gram of bismuth was added as nitrate to the same lead solution, the lead appeared to be held back by the bismuth, for, in order to obtain the same current, an anode potential of 1·30 volts had to be employed, and it was only when the bismuth was removed on the cathode that the potential of the anode could be reduced. It appears that the only explanation which may be given for this is that the lead combines with the bismuth in complex molecules (possibly also as complex ions) which require a higher anode potential for their oxidation than the molecules of pure lead nitrate. This matter is of considerable interest inasmuch as, so far as I am aware, we have hitherto had no evidence for the formation of complex molecules in solution between such substances as lead and bismuth nitrate.

The separation of bismuth from lead by graded potential of the cathode was then tried. In their *Analyse des Métaux par Electrolyse*, 1906, p. 90, Hollard and Bertiaux describe a method by which small quantities of bismuth may be separated from lead in forty-eight hours. The lead is made insoluble by converting it into the sulphate and adding alcohol. The bismuth is then deposited by the current. As has already been explained (p. 397), methods of this kind in which insoluble precipitates are suspended in the electrolyte are not suitable for the rotating electrodes used in the present investigation.

Attempts were made to separate bismuth from lead in tartrate and in nitrate solutions. The former failed as the bismuth always contained lead. The latter, however, were successful. Either glucose or tartaric acid was added to the solution to prevent the formation of lead peroxide on the anode. In the former case the deposit of bismuth was somewhat loose. This becomes especially noticeable when bismuth and copper are precipitated together (see p. 408). After the bismuth has been removed the lead is deposited from the same solution, but it was found necessary to weigh the anode as well as the cathode, as small quantities of lead peroxide were usually formed. Although very crystalline, the metal adhered sufficiently to allow it to be washed. When tartaric acid was employed as a reducing agent the deposit of bismuth was quite firm, but it was found necessary to make the solution ammoniacal for the deposition of the lead.

Experiments.—In experiments 1, 2, 3, the electrolyte contained about 2 c.c. of concentrated nitric acid and 15 grams of glucose, the volume being 85 c.c. during the precipitation of the bismuth; in experiment 4, 2 c.c. of concentrated nitric acid and 20 grams of glucose were employed. Owing to the large quantity of lead present in the latter experiment the metal was deposited in a form too loose for accurate determination (error 5 milligrams). The numbers in brackets represent the amount of lead found as peroxide on the anode. In experiment 5 the solution contained 1·6 c.c. of concentrated nitric acid and 15 grams of tartaric acid; in experiment 6, one c.c. of concentrated nitric acid and 20 grams of tartaric acid. In the latter case the solution was made strongly alkaline with 20 c.c. of concentrated ammonium hydroxide before the deposition of the lead. The second number represents the lead determined as peroxide by dissolving in nitric acid and reprecipitating:

No.	Taken.	Found.	Amps.	Volts anode-cathode.*	Volts auxiliary.	Temp.*	Time in minutes.
1.	0·3886 Bi	0·3900 Bi	3—0·2	—	0·42—0·55	60—70°	9
	0·3560 Pb	0·3552 Pb (3·8 mg.)	3	—	0·90—0·95	—	11
2.	0·3886 Bi	0·3903 Bi	3—0·2	1·8	0·43—0·55	60—70	11
	0·3560 Pb	0·3557 Pb	3	2·4	0·85—0·90	60—80	10
3.	0·3886 Bi	0·3892 Bi	3·5—0·2	1·9	0·42—0·55	70—80	11
	0·2856 Pb	0·2856 Pb (4·9 mg.)	3	2·2—2·6	—	65	15
4.	0·3109 Bi	0·3129 Bi	3—0·2	—	0·43—0·55	70	8
	0·7120 Pb	0·7076 Pb (23·1 mg.)	—	—	—	—	—
5.	0·3109 Bi	0·3123 Bi	3·5—0·2	—	0·45—0·55	75	8
	0·2848 Pb	—	—	—	—	—	—
6.	0·1554 Bi	0·1555 Bi	1·6—0·2	—	0·43—0·55	55—80	12
	0·2848 Pb	0·2853 Pb 0·2841 Pb	2	1·4	1·04—1·50	boiling	10

* Rough values.

Cadmium and its Separation from all the preceding Metals.—The estimation of cadmium on a rotating cathode has been examined in considerable detail by Flora (*loc. cit.*). For the purposes of the present investigation, it was thought specially desirable to be able to deposit the metal from nitrate solutions, and a considerable number of experiments were carried out for this purpose.

The only solutions in which the potential of the electrode could be pushed high enough for the complete deposition of the metal were neutral and alkaline ones, as the potential is kept too low in acid solutions by the reduction of the nitric acid. In order to obtain adherent deposits, the electrolyte must be strongly alkaline; the precipitates obtained from ammoniacal solutions are loose and useless. Experiments are quoted below for cyanide solutions, but the electrolyte principally used in the present investigation contained sodium tartrate. This liquid must be employed cold, as an insoluble, white precipitate from which it is very difficult to deposit the metal separates from hot solutions. When the current has passed for some time the solution appears to undergo a change, possibly in consequence of the formation of oxalic acid by oxidation of the tartrate, which either necessitates a very high potential of the cathode for the complete precipitation of the metal or makes it altogether impossible.

The method adopted to overcome this difficulty was to make the solution slightly ammoniacal at the end of the experiment, either by adding ammonium sulphate and boiling for some time until most of the ammonia had disappeared, or by first making the solution faintly acid and then faintly ammoniacal. Although the last traces of the metal separate in a slightly powdery state under these conditions, they adhere sufficiently to allow the deposit to be washed. As will be seen from the numbers given below, there is then a decided tendency for the results to be high, so that it may be desirable to redeposit the metal.

The great variability of the deposition-potential of metals in neutral and alkaline solutions containing organic substances (including cyanides) was a phenomenon generally observed. It is due to the changes which these substances undergo at the anode. In consequence these solutions are in general much less suited for separations by graded potential than acid ones, and the results obtained from them are not so trustworthy as the beautiful appearance of the deposits would lead one to expect.

Acetate solutions containing free acetic acid were employed for the separation of cadmium from zinc. The deposits are somewhat loose, and in consequence the results not trustworthy for very large quantities of metal. The largest amount accurately deposited was 0·15 gram. As has already been explained, nitrates must not be present in these acid electrolytes. All the depositions were carried out with a limited potential of the cathode.

Experiments.—In Nos. 1 and 2, cadmium was deposited on the cathode from a tartrate solution, weighed, then dissolved in an acid solution containing 2 c.c. of concentrated sulphuric acid, then 8 grams of sodium tartrate and 5 grams of sodium hydroxide were added, and the solution electrolysed until no cadmium could be detected by hydrogen sulphide. The subsequent experiments were either carried out with a solution made up from pure cadmium sulphate (Kahlbaum), and analysed according to the method proved correct by experiments 1 and 2, or with a solution prepared by dissolving a weighed quantity of electrolytically prepared cadmium in sulphuric acid. In No. 3, 2 c.c. of concentrated sulphuric acid and $3\frac{1}{3}$ grams of sodium hydroxide were added to the electrolyte, which was then acidified with $1\frac{1}{4}$ c.c. of glacial acetic acid. The quantities taken in No. 4 were 2 c.c. of concentrated sulphuric acid, $3\frac{1}{3}$ grams of sodium hydroxide, and 2 c.c. of acetic acid. In No. 5, 3 c.c. of concentrated sulphuric acid and 10 c.c. of concentrated ammonium hydroxide were added, and the solution was then acidified with $4\frac{1}{2}$ c.c. of glacial acetic acid:

No.	Cd taken.	Cd found.	Amps.	Volts anode–cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·3980	0·3983	5—0·3	2·9—2·3	1·45—1·60	cold	10
2.	0·4892	0·4890	5—0·3	—	1·45—1·60	,,	15
3.	0·1554	0·1554	4—1	2·6—2	1·12—1·20	80°	13
4.	0·1554	0·1547	3—1	—	1·12—1·20	70	—
5.	0·0777	0·770	2—0·4	—	1·15—1·20	45	8

Separation from the preceding Metals.—Cadmium is only deposited from acid solutions at a potential of the $2/N$ sulphuric acid electrode of more than 1 volt. Even when no auxiliary electrode is employed there is therefore no difficulty in hindering its precipitation by the addition of small quantities of nitric or large quantities of sulphuric acid. Of the metals dealt with in the present paper, the one nearest it in the electropotential series is lead; a separation from this metal therefore involves the separation from the rest. Results are also given below for bismuth. This was deposited either from a nitrate solution containing free nitric and tartaric acid or from a tartrate solution containing only free tartaric acid. In the former case, the potential of the auxiliary electrode was taken to 0·55 volt, in the latter to 0·70 volt. In both cases the current falls to about 0·2 volt when all the metal has been deposited. This does, however, not take place in the nitrate solutions if a reducing agent such as tartaric acid is not added.

For the separation of lead from cadmium a nitric acid solution was used containing glucose, and the potential of the auxiliary electrode was taken to 0·90 volt. The temperature should not be much below 60° and not above 80°. The current in this case does not fall to almost zero, but the course of the analysis may be readily followed if the approximate absence of lead is tested for by means of sulphuric acid. As a small amount of peroxide is generally deposited on the anode, the latter must be weighed before and after the experiment.

Experiments.—In No. 1, the solution contained 2½ c.c. of concentrated nitric acid and 18 grams of tartaric acid for the determination of the bismuth; before the determination of the cadmium it was made alkaline with 17 grams of sodium hydroxide. In No. 2, the quantities were 2½ c.c. of concentrated nitric acid and 12 grams of tartaric acid. In No. 3, the solution for the deposition of bismuth was identical with No. 2; for the determination of the cadmium it was made strongly alkaline with 3½ grams of sodium hydroxide, the deposition of the latter metal was carried on for ten minutes in the cold, then 15 grams of ammonium sulphate were added, and the electrolysis continued in a boiling solution for nine minutes. In experiment 4, the solutions were identical with No. 3, but during the deposition of the cadmium the electrolyte was heated; in consequence it became turbid, 15 grams of ammonium sulphate were then added, but a considerable time was required to make the solution clear again.

In experiment 5, the solution contained 0·25 c.c. of concentrated nitric acid and 15 grams of glucose for the determination of the lead; before the estimation of the cadmium it was made alkaline with 3⅓ grams of sodium hydroxide, and two-thirds of a gram of potassium cyanide was added.

In experiment 6, the solution for the determination of the lead was the same as in No. 5; for the estimation of the cadmium 8 grams of sodium tartrate and 3½ grams of sodium hydroxide were added, the electrolysis was carried on for 30 minutes in the cold, and then continued at boiling temperature. The numbers in brackets give the weight of lead found as peroxide on the anode (dried only by alcohol and ether). In all these experiments the cadmium was deposited until constant in weight.

No.	Taken.	Found.	Amps.	Volts anode–cathode.*	Volts auxiliary.	Temp.*	Time in minutes.
1.	0·3886 Bi	0·3878 Bi	3—0·2	1·7	0·43—0·55	80°	10
	0·3887 Cd	0·3880 Cd	2	2·7	—	cold	18
2.	0·3886 Bi	0·3886 Bi	3—0·2	—	0·60—0·70	boiling	7
	0·3887 Cd	—	—	—	—	—	—
3.	0·3886 Bi	0·3867 Bi	3—0·2	1·4	0·60—0·70	boiling	7
	0·3887 Cd	0·3905 Cd	3	3	—	cold, then boiling	19
4.	0·3886 Bi	0·3884 Bi	3—0·2	1·6	0·60—0·75	80°	10
	0·3887 Cd	0·3862	—	—	—	—	—
5.	0·2848 Pb	0·2841 Pb (0·5 mg.)	3—1·8	2·7	0·80—0·90	70°	12
	0·3752 Cd	0·3771 Cd	3	3·8—4·5	1·40—2·00	cold	55
6.	0·2848 Pb	0·2846 Pb (1·0 mg.)	3—1·2	—	0·83—0·90	80	10
	0·3752 Cd	0·3787 Cd	3	3·5	—	cold, then boiling	55

* Rough values.

Zinc and its Separation from all the Preceding Metals, and the Electrolytic Destruction of Nitric Acid in Solution.

It appears that the potential at which zinc is deposited from all its solutions is too high to allow it to be quantitatively estimated in the presence of nitrates. When the solution contains nitric acid, the latter must therefore be removed, before the precipitation of the zinc, either by evaporation with sulphuric acid or by reduction to ammonia. The former process is somewhat lengthy, and besides would be quite unsuitable in the presence of considerable quantities of organic substances such as glucose or tartaric acid. A series of experiments was therefore carried out for the purpose of determining the most suitable conditions for the rapid electrolytic reduction of nitric acid to ammonia.

It was shown by Luckow (*Zeitsch. anal. Chem.*, 1880, **19**, 11) that the presence of copper on the cathode catalytically causes this reduction to take place when an electric current is passed through a solution containing nitric and sulphuric acids, and since that time several investigations have been carried out, mainly with the object of employing this reaction for the estimation of nitric acid (see Vortmann, *Ber.*, 1890, **23**, 2798); Ulsch (*Zeitsch. Elektrochem.*, 1897, **3**, 546); Ingham (*J. Amer. Chem. Soc.*, 1904, **26**, 1251).

The method chosen in the present investigation consisted in depositing about 0·3 gram of spongy copper on the cathode. A sulphuric acid solution was employed for this purpose containing a large quantity of glucose, and the copper was deposited by a strong current in the cold, the stirrer moving slowly. This operation could be effected either in the electrolyte containing the nitric acid or in a separate solution. The reduction of the nitric acid was effected slightly below the boiling point of the solution by a strong current, the stirrer moving slowly. It is possible to follow the process by means of the auxiliary electrode, the potential of which rises from about 0·5 to 0·8 or 0·9 volt as the nitric acid is destroyed. The disappearance of the latter may be ascertained by the diphenylamine test.

Example.—Spongy copper was deposited from 250 c.c. of a solution containing 0·3 gram of copper as sulphate, 1½ c.c. of concentrated sulphuric acid and 15 grams of glucose, by a current of 10 amperes in three minutes.

The reduction of 1 c.c. of concentrated nitric acid in 100 c.c. of water containing 2 c.c. of concentrated sulphuric acid took place by means of the electrode prepared thus in twenty-three minutes slightly below the boiling point of the solution with a current of 10 amperes. During this process the potential of the auxiliary electrode rose from 0·52 to 0·80 volt. The stirrer was moving slowly.

Zinc.—For the determination of zinc, Exner (*loc. cit.*) recommended acetate and sodium zincate solutions. The only electrolyte employed in the present investigation was an acetate solution containing a small amount of free acetic acid. Alkali sulphates were always added, as these may be considered to be present in all practical cases. It was found difficult to deposit the last traces of zinc at temperatures much above 30°. As the electrolyte is usually heated above this temperature in consequence of the passage of the current, the beaker was in some of the experiments placed in a large dish containing cold water. The results show a slight tendency to be high.

Experiments.—A weighed quantity of purest zinc was dissolved in sulphuric acid, the slight residue filtered off, weighed, and found almost negligible; the solution was made up to a known volume and measured quantities taken.

In each experiment sulphuric acid was first added to the solution; it was then made strongly alkaline with either sodium- or ammonium-hydroxide and then acidified with acetic acid. In a few cases ammonium acetate was also added. The quantities taken are given in the following table. In the table of results, the second number under zinc found represents the value obtained on depositing the metal to constant weight. For all these experiments the cathode was plated with copper:

No.	H_2SO_4 in c.c.	NaOH in grams.	Concentrated NH_4·OH in c.c.	Glacial HAc in c.c.	NH_4Ac in grams.
1.	1½	3⅓	—	1⅓	—
2.	1¼	6⅔	—	9	—
3.	3	5½	—	1¼	—
4.	1¼	—	10	8	—
5.	1¼	—	10	8	—
6.	1¼	—	3½	1⅓	2½
7.	1¼	—	4½	2½	2½

No.	Zn taken.	Zn found.	Amps.	Volts anode-cathode.	Volts auxiliary.	Temp.	Time in minutes.
1.	0·6175	0·6168	3	4—4·5	—	cold	30
2.	0·4943	0·4957	3	3·8—4	1·45—1·70	,,	18
3.	0·2529	0·2540	3—4	3·6—4·2	1·45—1·50	,,	13
4.	0·4943	0·4944 0·4957	3	3·8—4·3	1·50—1·55	,,	20 + 10
5.	0·4943	0·4946 0·4953	3	3·8—4·3	—	,,	20 + 10
6.	0·4943	0·4944	3	—	—	,,	30
7.	0·4943	0·4938 0·4945	3—4	3·6—4·2	—	,,	20 + 10

Separation from the preceding Metals.—As is known, there is no difficulty in separating zinc from the majority of the preceding metals in consequence of the high potential required for its deposition. Cadmium being the metal preceding it in the electropotential series, a separation from this metal in acid solution involves the separation from all the others. It was stated by Freudenberg (*loc. cit.*) that a separation of cadmium from zinc could be effected in alkaline cyanide solutions, but for the reasons stated above (p. 401), it seems doubtful whether trust can be placed on a method of this kind.

Several successful experiments were carried out in which cadmium was separated from zinc in a weak acetic acid solution at a potential of the auxiliary electrode limited to 1·20 volts. Attention should, however, be drawn here to two experiments in which the cadmium contained some zinc, and I have not yet succeeded in explaining them. The experiments were Nos. 4 and 5 of p. 400 in the paragraph on the separation of seven metals from one solution. The conditions were a low temperature (about 15—20°) and a slightly rough cathode as a result of dissolving the combined metals cadmium and zinc immediately before the deposition of the cadmium, possibly also as a result of the presence of a trace of spongy copper. This led to a considerable evolution of hydrogen at the potential at which the cadmium was deposited.

Our present knowledge will, so far as I can see, not afford an explanation, but the following interpretation may be put forward tentatively as the result of a preliminary experiment. If hydrogen is liberated simultaneously with zinc, the latter may be deposited, especially at low temperatures, at a much lower potential than that at which it is in equilibrium with its solutions. The metal is probably deposited primarily as a hydride at a potential intermediate between the equilibrium potentials of hydrogen and zinc. In the two experiments referred to, the electrode with the cadmium was replaced in the solution from which the latter had been deposited, so that the greater part of the metal passed into solution again. It was then redeposited at about 30°, giving the correct result quoted on p. 410.

Experiments.—The following reagents were added to the electrolyte. In Nos. 1 and 2, 2 c.c. of concentrated sulphuric acid, 3⅓ grams of sodium hydroxide, and 1 c.c. of glacial acetic acid; in Nos. 3 and 4, 2 c.c. of concentrated sulphuric acid, 4 grams of sodium hydroxide, 1 gram of ammonium acetate, and 1½ c.c. of glacial acetic acid:

No.	Taken.	Found.	Amps.	Volts anode–cathode.*	Volts auxiliary.	Temp.*	Time in minutes.
1.	0·0777 Cd	0·0778 Cd	2—0·8	2·7	1·15—1·20	cold	11
	0·4943 Zn	0·4938 Zn	4	4·5	—	,,	20
2.	0·0777 Cd	0·0770 Cd	2·4—1	3—2·6	1·15—1·20	30°	12
	0·4943 Zn	0·4958 Zn	3	4·3	—	—	25
3.	0·0777 Cd	0·0770 Cd	2—0·5	—	1·15—1·20	35	12
	0·2514 Zn	—	—	—	—	—	—
4.	0·0777 Cd	0·0775 Cd	1·2—0·3	3—2·6	1·15—1·20	37	12
	0·2514 Zn	—	—	—	—	—	—

* Rough values.

The Rapid Separation of more than Two Metals from One Solution.

The difficulties met with in the rapid separation of a large number of metals from one solution are twofold. Firstly, the solution may become so much diluted by the wash-waters that it may be necessary to concentrate it by evaporation, involving loss of time. Secondly, a more serious difficulty is met with when large quantities of organic substances are present which by their oxidation may lead to the formation of compounds which either by chemical combination or owing to their viscid nature may retard the deposition of the other metals. As a rule, it will therefore be found best to precipitate more than one metal at a time and redissolve and separate the mixture.

If possible, the use of organic substances should be avoided in those solutions from which more than two metals are to be precipitated. The records of the following experiments will illustrate these remarks.

a. *Three Metals in One Solution. Lead, Cadmium, and Zinc.*

In experiment 1 a solution of the nitrates was taken containing about 0·2 c.c. of free nitric acid, 15 grams of glucose were added and the lead was precipitated as metal on the cathode (p. 402). The potential of the auxiliary electrode was taken to 0·90 volt, and the duration of the experiment was seven minutes. The number in brackets was the amount found on the anode as peroxide. The nitric acid was then destroyed (p. 404) in twenty-seven minutes, 2 c.c. of concentrated sulphuric acid and 0·3 gram of copper as sulphate having been added to the electrolyte. After the reduction of the nitric acid, the electrode was allowed to stand for several minutes in the acid liquid to allow any cadmium which might have been precipitated on the copper to pass into solution. The liquid was then filtered from particles of the spongy copper which had fallen off the electrode. Traces of copper which had gone into solution were deposited on the cathode in five minutes at a potential of the auxiliary electrode of 0·40 to 0·60 volt. The free sulphuric acid was then replaced by acetic acid by the addition of $6\frac{2}{3}$ grams of sodium hydroxide and 2 c.c. of glacial acetic acid, and the cadmium and zinc precipitated together from the cooled liquid. The combined precipitate was then dissolved in a solution to which 1·2 c.c. of concentrated sulphuric acid was gradually added, and the cadmium deposited after the addition of $3\frac{1}{3}$ grams of sodium hydroxide and $3\frac{1}{2}$ c.c. of glacial acetic acid. The potential of the auxiliary electrode was taken to 1·20 volts, and the duration of the experiment was twelve minutes. From the remaining liquid the zinc was deposited by 3 amperes in half an hour. Experiment 2 is an earlier determination in which all the metals were deposited in succession from the same liquid :

	Pb.	Cd.	Zn.
Taken …………	0·1424	0·938	0·2574
Found, No. 1 …	0·1416 (1·0 mg.)	0·948	0·2581
Found, No. 2 …	0·1424 (1·7 mg.)	0·936	0·2605

b. *Four Metals in One Solution. Copper, Bismuth, Lead, and Cadmium.*

Experiment 3.—A solution of the nitrates was taken containing nearly 1 c.c. of free nitric acid. The solution was first electrolysed at 60°, the potential of the auxiliary electrode being taken from

0·35—0·55 volt. Practically the whole of the lead and part of the bismuth were deposited on the anode, and all the copper and the rest of the bismuth on the cathode. As the current did not fall to zero, a much longer time than was probably necessary for the deposition, namely, twenty minutes, was employed. The cathode was then weighed, and the bismuth in the deposit determined according to the cyanide-tartrate method (p. 396), the electrolysis being continued for nineteen minutes. This gave the weight of the copper by difference. Before this determination the deposit on the anode had been completely dissolved in a solution containing 2 c.c. of concentrated nitric acid and 20 grams of tartaric acid at slightly below the boiling point, and from this liquid the remaining bismuth was deposited on the first portion according to experiments 5 and 6, p. 400. The lead was next deposited as metal (p. 400, No. 6), and the result checked by dissolving it in nitric acid and depositing on the anode (second figure given).

In the liquid remaining from the first operation, the cadmium was determined according to experiment 6, p. 403. It was then dissolved in nitric acid and the trace of lead present deposited on the anode. The correction found for lead amounted to 0·8 milligram :

	Cu.	Bi.	Pb.	Cd.
Taken	0·3682	0·1554	0·1424	0·0938
Found	0·3702	0·1534	0·1438 0·1427	0·0945

c. *Seven Metals in one Solution. Silver, Mercury, Copper, Bismuth, Lead, Cadmium, and Zinc.*

Experiment 4.—In this experiment, much difficulty was experienced from the causes outlined above. It was attempted to prevent the precipitation of the lead on the anode by the addition of 16 grams of glucose at the beginning of the experiment. The silver and mercury were first precipitated together and then separated from each other as described on p. 390, the potential of the auxiliary electrode being taken to 0·15 volt, and the mercury employed for plating the cathode amounting to about 2½ grams. From the remaining liquid, the copper and bismuth were precipitated together and then separated as described on p. 396. Owing to the presence of the glucose, both the first deposits were somewhat loose. In consequence, small particles of metal were seen in the wash-waters. These were filtered off, dissolved in nitric acid added to the original solutions, and corrections made by precipitating the traces left in the same way as the first two deposits. The corrections were 1·6 and 3·6 milligrams. After this, the solution had become so dilute that it was thought advisable to concentrate it by partial evaporation. It had, however, become so much charged with decomposition products of the sugar that the lead was not completely deposited at its proper potential. The nitric acid in the solution was reduced electrolytically as described on p. 404, and all the remaining metals were precipitated as completely as possible. The deposit thus obtained was dissolved in sulphuric acid and the cadmium separated from the zinc (see p. 405). The results for cadmium marked with an asterisk in experiments 4 and 5 are the second obtained, the first having been nearly a centigram too high in both cases. This was probably a result of the rough surface of the electrode left after the solution of the zinc combined with the low temperature employed. All the zinc was not precipitated, the presence of the large amount of decomposition products of the sugar having evidently made its complete deposition impossible. The amount obtained is the first number on the table. It was then attempted to obtain the remainder by adding ammonia and ammonium sulphide to the solution and allowing it to stand for several days at about 40°. The small amount of sulphide which separated out was collected and the zinc determined electrolytically, the weight being added to the first result (second number given). Even with this correction the result is low. The copper employed for the electrolytic reduction of the nitric acid and the cadmium were both examined electrolytically for lead. In the former, 2·3 milligrams were found, and this number was added to the result originally obtained, giving the number quoted.

Experiment 5.—The amount of free concentrated nitric acid present in the solution was again slightly less than 1 c.c. No organic substance was added to the electrolyte, but the separation was carried out in a manner similar to experiment 3 on p. 407. In the first deposition, the potential of the auxiliary electrode was taken to 0·15 volt in a boiling solution. This gave the silver and mercury on the cathode and hardly any lead on the anode. The cathode was plated with mercury for this deposition as in the previous experiment. The second deposition, in which the potential of the auxiliary electrode was taken to 0·55 volt, gave nearly all the lead and part of the bismuth on the anode, all the copper and the rest of the bismuth on the cathode. These deposits were treated as in experiment 3. The nitric acid was reduced electrolytically, and the zinc and cadmium first deposited together and then separated as in the preceding experiment 4. The same difficulty was again met with. The traces of lead which did not separate at the anode in the second deposition were recovered electrolytically as peroxide from the cadmium.

Experiment 6.—This experiment was carried out as No. 5, but the roughening of the cathode immediately before the precipitation of the cadmium which arose out of the method of working in the preceding experiments was avoided. After the deposition of the copper, bismuth, and lead, the nitric acid was expelled by evaporating the electrolyte almost to dryness on the water-bath with 3 c.c. of concentrated sulphuric acid. In the residue, the cadmium and zinc were determined as described on p. 405. In experiments 5 and 6, the results for lead were checked by dissolving the metal and redepositing it as peroxide. Both numbers are quoted.

No difficulty was encountered in experiment 6. The times of deposition were: silver *plus* mercury, 10 minutes; silver, 8 minutes; lead and part of the bismuth on the anode, copper and the rest of the bismuth on the cathode, 15 minutes; separation of the bismuth from the combined deposits of copper and bismuth, 15 minutes; separation of the rest of the bismuth from the combined peroxides of lead and bismuth, 10 minutes; lead as metal, 7 minutes; as peroxide, 10 minutes; cadmium, 15 minutes; zinc, 15 minutes; examination of the cadmium for traces of lead, 5 minutes.

Results of Experiments 4, 5, *and* 6.

No.		Ag + Hg.	Ag.	Cu.	Bi.	Pb.	Cd.	Zn.
	Taken...	0·2244	0·1078	0·1841	0·1554	0·1424	0·0938	0·1287
4.	Found...	0·2231	0·1099	0·1861	0·1557	0·1401	0·0949 *	0·1175 0·1228
	Taken...	0·2244	0·1078	0·3682	0·1554	0·1424	0·0938	0·1287
5.	Found...	0·2247	—	0·3696	0·1552	0·1461 0·1429	0·0935 *	0·1289
6.	Found...	0·2249	0·1098	0·3682	0·1548	0·1455 0·1441	0·0935	0·1311

In conclusion, it should be again pointed out that the electrodes here described may be used without an auxiliary electrode in all the cases of separation by graded potential which give trustworthy results by the slow methods hitherto known. Owing to their small resistance, they allow a current to be employed, even under this condition, which is sufficient to permit the metals to be deposited in a small number of minutes.

A part of the expense incurred in this investigation has been met by a grant awarded by the Government Grant Committee of the Royal Society, for which the author desires to express his thanks.

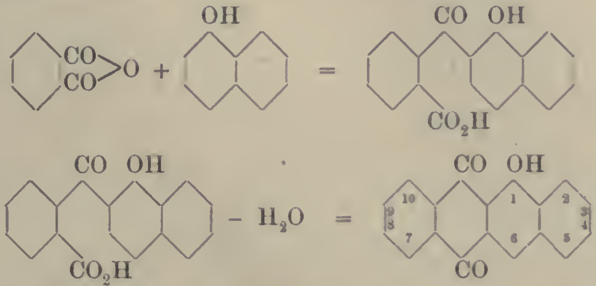
University College,
Nottingham.

XLII.—*Derivatives of Naphthacenequinone.*

By William Henry Bentley, Arthur Friedl, Frederick Thomas, and Charles Weizmann.

Introduction.

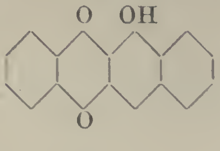
1-Hydroxynaphthacenequinone was first prepared by the action of sulphuric and boric acids on a mixture of phthalic anhydride and α-naphthol (Deichler and Weizmann, *Ber.*, 1903, **36**, 547), the reaction proceeding in two stages with the intermediate formation of hydroxynaphthylbenzoic acid:



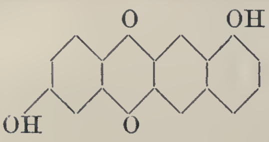
In view of the analogy existing between hydroxynaphthacenequinone and hydroxyanthraquinone, it seemed of great interest to us to study the effect of substituent groups in both the naphthalene and the benzene nucleus of 1-hydroxynaphthacenequinone.

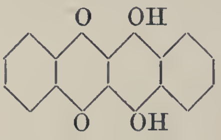
With this object we have prepared numerous derivatives, firstly by direct substitution in 1-hydroxynaphthacenequinone itself (or in α-hydroxy-β-naphthoylbenzoic acid), and secondly by the condensation of derivatives of phthalic anhydride with derivatives of α-naphthol.

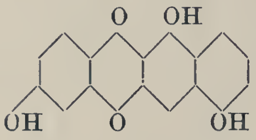
The present communication deals mainly with the hydroxy- and amino-derivatives of 1-hydroxynaphthacenequinone, and our study of these compounds has led us to the general conclusion that the substituent auxochromic group exerts a much greater influence on the colour when in the naphthalene than when in the benzene nucleus of the naphthacenequinone molecule. This is at once apparent when the colour of the caustic alkaline solutions of the hydroxynaphthacenequinone is observed. Thus the alkaline solution of

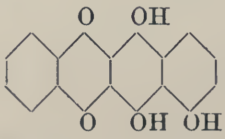


is bluish-red

of  is yellowish-red

of  is deep bluish-violet

of  is red

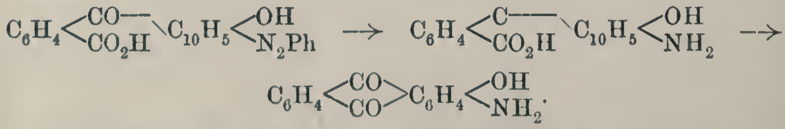
and of  is indigo-blue.

It would appear that in the benzene nucleus, the introduction of a hydroxyl group, instead of increasing, actually has a weakening effect on the colour of naphthacenequinone derivatives.

So far as the naphthalene nucleus is concerned, the amino-group acts like the hydroxyl group in deepening the colour, but we have not yet studied its effect when substituted in the benzene nucleus.

1-*Aminonaphthacenequinone* was found easy to prepare by the action of ammonia on 1-hydroxynaphthacenequinone at 200°.

1-*Amino-6-hydroxynaphthacenequinone* was obtained by elimination of water from aminohydroxynaphthoylbenzoic acid. The latter can be easily prepared by reducing the benzeneazo-derivative of hydroxynaphthoylbenzoic acid:



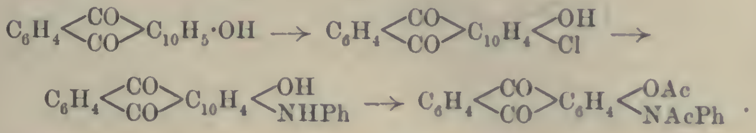
$$C_6H_4<\begin{matrix}CO—\\CO_2H\end{matrix}\diagdown C_{10}H_5<\begin{matrix}OH\\N_2Ph\end{matrix} \longrightarrow C_6H_4<\begin{matrix}C——\\CO_2H\end{matrix}\diagdown C_{10}H_5<\begin{matrix}OH\\NH_2\end{matrix} \longrightarrow$$

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4<\begin{matrix}OH\\NH_2\end{matrix}.$$

This condensation takes place with considerable ease, it being only necessary to heat the acid alone or with a solvent of high boiling point, such as nitrobenzene. When the acid is heated with concentrated sulphuric acid the quinone formed is sulphonated, yielding a violet dye-stuff. This dye-stuff, when fused with caustic potash, yields a trihydroxynaphthacenequinone, the amino-group being replaced by hydroxyl.

1-Hydroxynaphthacenequinone, although not affected by chlorine at low temperatures, yields a monochloro-derivative, at temperatures between 200° and 300°, which is probably 1-*chloro-6-hydroxynaphthacenequinone.* This substance when boiled with aniline yields an anilino-derivative which dissolves in sulphuric acid, forming a reddish-yellow, fluorescent solution indicating the possible formation of an acridine derivative.

Anilinohydroxynaphthacenequinone forms dark brown crystals of a metallic lustre, and on treatment with acetic anhydride yields a yellow diacetyl derivative:

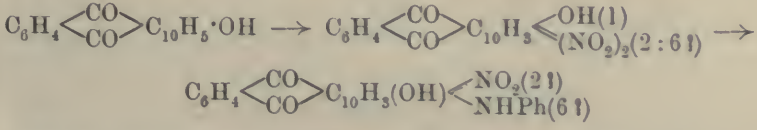


$$C_6H_4 < \substack{CO \\ CO} > C_{10}H_5{\cdot}OH \longrightarrow C_6H_4 < \substack{CO \\ CO} > C_{10}H_4 < \substack{OH \\ Cl} \longrightarrow$$

$$C_6H_4 < \substack{CO \\ CO} > C_{10}H_4 < \substack{OH \\ NHPh} \longrightarrow C_6H_4 < \substack{CO \\ CO} > C_6H_4 < \substack{OAc \\ NAcPh} .$$

Considerable difficulty was experienced in the nitration of 1-hydroxynaphthacenequinone, the product usually consisting of an intimate mixture of nitro-compounds which could only be separated by tedious methods.

The presence of boric acid, however, during the nitration led to the formation of a much simpler product, and in this way *dinitrohydroxynaphthacenequinone* was readily obtained pure. The restraining influence of boric acid is very remarkable, and is known to be of considerable importance in the manufacture of alizarin derivatives. It is probably due to the formation of a boric ester. When this dinitro-compound is boiled with aniline it loses one nitro-group, with the formation of the corresponding anilino-derivative:

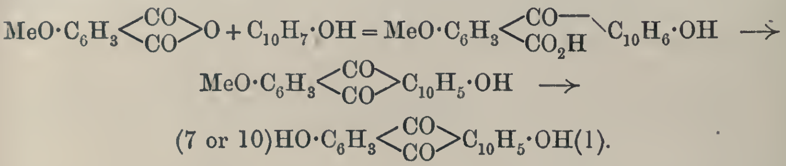


$$C_6H_4 < \substack{CO \\ CO} > C_{10}H_5{\cdot}OH \longrightarrow C_6H_4 < \substack{CO \\ CO} > C_{10}H_3 \lessgtr \substack{OH(1) \\ (NO_2)_2(2:6?)} \longrightarrow$$

$$C_6H_4 < \substack{CO \\ CO} > C_{10}H_3(OH) < \substack{NO_2(2?) \\ NHPh(6?)}$$

When treated with concentrated sulphuric acid, dinitrohydroxynaphthacenequinone yields a mixture of blue and violet dye-stuffs which belong to the class of aminohydroxynaphthacenequinones and are similar to the compounds obtained when dinitroanthraquinone is treated with sulphuric acid. The separation and examination of these interesting derivatives will be the subject of a future publication.

When 3 methoxyphthalic anhydride and α-naphthol are fused with boric acid condensation takes place, and 1′-hydroxy-3(6)-methoxy-2-β-naphthoylbenzoic acid (m. p. 210—215°) is produced. This acid dissolves in warm sulphuric and boric acids with elimination of water and formation of the quinone, as is seen by the deep brown colour. This colour changes, on further heating, to a reddish-violet, and the solution becomes strongly fluorescent, a change which is due to hydrolysis, to 1 : 7(10)-dihydroxynaphthacenequinone (m. p. 280—300°) in sulphuric acid solution :

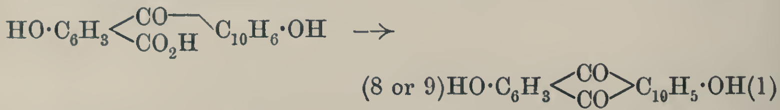


$$\mathrm{MeO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}}\Big>\mathrm{O}+\mathrm{C_{10}H_7{\cdot}OH}=\mathrm{MeO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\!-\!\!-\\ \mathrm{CO_2H}\end{matrix}}\diagdown\mathrm{C_{10}H_6{\cdot}OH}\longrightarrow$$

$$\mathrm{MeO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}}\Big>\mathrm{C_{10}H_5{\cdot}OH}\longrightarrow$$

$$\mathrm{(7\ or\ 10)HO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}}\Big>\mathrm{C_{10}H_5{\cdot}OH(1)}.$$

In a similar manner, 4-hydroxyphthalic acid yields 4(5):1′-dihydroxy-2-β-naphthoylbenzoic acid (m. p. 215—216°), which condenses when heated with boric and sulphuric acids to the corresponding 1 : 8(9)-dihydroxynaphthacenequinone :

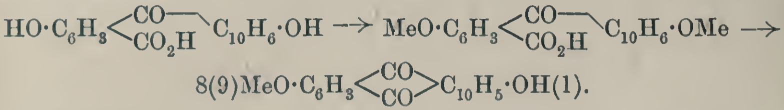


$$\mathrm{HO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\!-\!\!-\\ \mathrm{CO_2H}\end{matrix}}\diagdown\mathrm{C_{10}H_6{\cdot}OH}\longrightarrow$$

$$\mathrm{(8\ or\ 9)HO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}}\Big>\mathrm{C_{10}H_5{\cdot}OH(1)}$$

(compare Levinsohn, "Acides Oxynaphthoylbenzoïques," Genève, 1903).

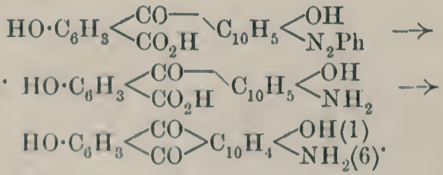
4(5) : 1′-*Dihydroxy-2-β-naphthoylbenzoic acid* * is readily methylated with dimethylsulphate and caustic potash, yielding 4(5) : 1′-*dimethoxynaphthoylbenzoic acid* (m. p. 195—197°), which dissolves in warm sulphuric and boric acids with condensation and partial hydrolysis to *hydroxymethoxynaphthacenequinone*, a crystalline yellow powder melting at about 250°. These changes may probably be represented thus :



$$\mathrm{HO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\!-\!\!-\\ \mathrm{CO_2H}\end{matrix}}\diagdown\mathrm{C_{10}H_6{\cdot}OH}\longrightarrow\mathrm{MeO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\!-\!\!-\\ \mathrm{CO_2H}\end{matrix}}\diagdown\mathrm{C_{10}H_6{\cdot}OMe}\longrightarrow$$

$$\mathrm{8(9)MeO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}}\Big>\mathrm{C_{10}H_5{\cdot}OH(1)}.$$

4(5) : 1′-Dihydroxy-2-β-naphthoylbenzoic acid combines in alkaline solution with diazobenzene chloride, producing an azo-derivative which, on reduction, yields 4′-amino-1′ : 4(5)-dihydroxy-2-β-naphthoylbenzoic acid. This amino-acid easily condenses on heating alone or with nitrobenzene, or even acetic acid, with formation of aminodihydroxynaphthacenequinone :



$$\mathrm{HO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\!-\!\!-\\ \mathrm{CO_2H}\end{matrix}}\diagdown\mathrm{C_{10}H_5}\Big<{\begin{matrix}\mathrm{OH}\\ \mathrm{N_2Ph}\end{matrix}}\longrightarrow$$

$$\mathrm{HO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\!-\!\!-\\ \mathrm{CO_2H}\end{matrix}}\diagdown\mathrm{C_{10}H_5}\Big<{\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}}\longrightarrow$$

$$\mathrm{HO{\cdot}C_6H_3}\Big<{\begin{matrix}\mathrm{CO}\\ \mathrm{CO}\end{matrix}}\Big>\mathrm{C_{10}H_4}\Big<{\begin{matrix}\mathrm{OH(1)}\\ \mathrm{NH_2(6)}\end{matrix}}.$$

4′-Bromo-1′ : 4(5)-dihydroxy-2-β-naphthoylbenzoic acid is obtained

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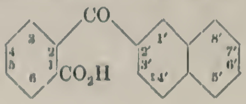
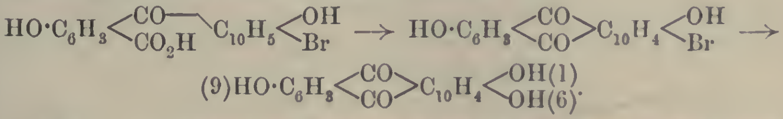
* Method of nomenclature :



when dihydroxynaphthoylbenzoic acid is treated with bromine in the presence of carbon disulphide; when heated with boric and sulphuric acids to 180°, it evolves hydrogen bromide and bromine, and yields a quinone which is doubtless trihydroxynaphthacenequinone compare Orchardson and Weizmann, Trans., 1906, 89, 115):

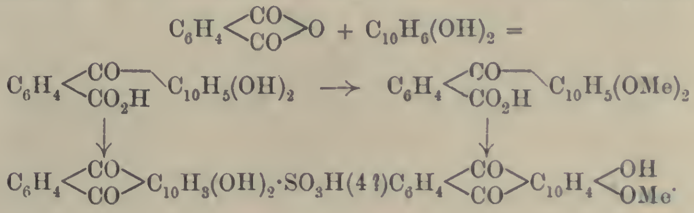


$$\mathrm{HO\cdot C_6H_3}<\begin{smallmatrix}\mathrm{CO}-\!\!-\\\mathrm{CO_2H}\end{smallmatrix}\diagdown\mathrm{C_{10}H_5}<\begin{smallmatrix}\mathrm{OH}\\\mathrm{Br}\end{smallmatrix}\longrightarrow\mathrm{HO\cdot C_6H_3}<\begin{smallmatrix}\mathrm{CO}\\\mathrm{CO}\end{smallmatrix}>\mathrm{C_{10}H_4}<\begin{smallmatrix}\mathrm{OH}\\\mathrm{Br}\end{smallmatrix}\longrightarrow$$

$$\mathrm{(9)HO\cdot C_6H_3}<\begin{smallmatrix}\mathrm{CO}\\\mathrm{CO}\end{smallmatrix}>\mathrm{C_{10}H_4}<\begin{smallmatrix}\mathrm{OH(1)}\\\mathrm{OH(6)}\end{smallmatrix}.$$

When 1:5-dihydroxynaphthalene is heated with phthalic anhydride and boric acid, it yields 1′:5′-dihydroxy-2-β-naphthoylbenzoic acid (m. p. 221°), which can be readily methylated with dimethylsulphate and caustic potash with the formation of 1′:5′-dimethoxy-2-β-naphthoylbenzoic methyl ester. The latter on hydrolysis with caustic potash yields 1′:5′-dimethoxy-2-β-naphthoylbenzoic acid (m. p 209—210°).

1′:5′-Dihydroxy-2-β-naphthoylbenzoic acid, when heated with boric and sulphuric acids, condenses to the corresponding quinone, which at the same time becomes sulphonated, whereas 1′:5′-dimethoxy-2-β-naphthoylbenzoic acid, under similar treatment, condenses without sulphonation, but with the hydrolysis of one of the methoxy-groups:



$$\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{CO}\\\mathrm{CO}\end{smallmatrix}>\mathrm{O}+\mathrm{C_{10}H_6(OH)_2}=$$

$$\begin{array}{ccc}\mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{CO}-\!\!-\\\mathrm{CO_2H}\end{smallmatrix}\diagdown\mathrm{C_{10}H_5(OH)_2} & \longrightarrow & \mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{CO}-\!\!-\\\mathrm{CO_2H}\end{smallmatrix}\diagdown\mathrm{C_{10}H_5(OMe)_2}\\ \downarrow & & \downarrow\\ \mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{CO}\\\mathrm{CO}\end{smallmatrix}>\mathrm{C_{10}H_3(OH)_2\cdot SO_3H(4?)} & & \mathrm{C_6H_4}<\begin{smallmatrix}\mathrm{CO}\\\mathrm{CO}\end{smallmatrix}>\mathrm{C_{10}H_4}<\begin{smallmatrix}\mathrm{OH}\\\mathrm{OMe}\end{smallmatrix}.\end{array}$$

EXPERIMENTAL.

1-*Aminonaphthacenequinone.*

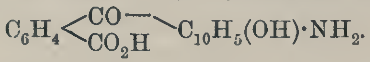
This substance is easily prepared from 1-hydroxynaphthacenequinone either by heating it in the autoclave with strong aqueous ammonia to 200° for three hours, or by the action of a stream of dry ammonia gas at 200—300°. The product from either process is collected, dried, and crystallised from nitrobenzene, from which it separates in beautiful, deep-brown needles (m. p. 290—292°):

0·1511 gave 0·4399 CO_2 and 0·0502 H_2O. C = 79·39; H = 3·69.
0·2073 „ 9·4 c.c. at 15° and 748 mm. N = 5·30.
$C_{18}H_{11}O_2N$ requires C = 79·12; H = 4·03; N = 5·13 per cent.

1-*Aminonaphthacenequinone* dissolves easily in cold concentrated sulphuric acid with an intense bluish-red colour, and is precipitated unchanged on the addition of water. Treated with potassium bichromate in acetic acid solution, it yields a yellow substance which dissolves in alcoholic potash with a red colour and is therefore possibly a diquinone.

1-Aminonaphthacenequinone is converted into an orange dye-stuff (on mordanted wool) by heating with fuming sulphuric acid. Apparently Liebermann and Kostanecki's rule (*Ber.*, 1901, **34**, 2344; 1902, **35**, 11,490) cannot be applied to the naphthalenequinone series, as we have already found several mordant dye-stuffs in this group which do not contain two hydroxyls in the ortho-position.

4′-*Amino*-1′-*hydroxy*-2-β-*naphthoylbenzoic acid*,



$$C_6H_4<\begin{matrix}CO-\\CO_2H\end{matrix}>C_{10}H_5(OH)\cdot NH_2.$$

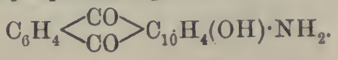
A considerable quantity of this substance was obtained by the reduction of benzeneazohydroxynaphthoylbenzoic acid, which can be prepared in the following manner.

1′-Hydroxynaphthoylbenzoic acid (185 grams) is dissolved in water (2 litres) containing caustic soda (80 grams); to this solution (cooled to 5°) is added during continuous agitation a solution of diazobenzene chloride prepared from the calculated quantity of aniline (59 grams). The sodium salt of the azo-compound separates as a yellowish-red precipitate and is collected, ground into a paste with a little water and mixed with a solution of stannous chloride (285 grams) in concentrated hydrochloric acid (750 c.c.). The mixture is heated on the water-bath for several hours, when the colour changes to grey. The precipitate is then collected, washed with hydrochloric acid and afterwards with water. In order completely to remove tin compounds the product is dissolved in sodium carbonate, the filtered solution acidified with hydrochloric acid, and the grey precipitate collected and purified by crystallising from alcohol:

0·1151 gave 0·2657 CO_2 and 0·0425 H_2O. C = 62·96; H = 4·10.
0·2132 „ 7·8 c.c. nitrogen at 15° and 746 mm. N = 4·20.
0·1354 „ 0·0737 AgCl. Cl = 13·47.
$C_{18}H_{13}O_4N,HCl$ requires C = 62·88; H = 4 08; N = 4·08; Cl = 10·3
per cent.

4′-*Amino*-1′-*hydroxy*-2-β-*naphthoylbenzoic acid* is soluble in sodium carbonate with a deep brown colour. It is only sparingly soluble in alcohol or benzene; in hot acetic acid it dissolves, being partly converted into the quinone (see later).

1-*Amino-6-hydroxynaphthacenequinone*,



$$C_6H_4{<}\substack{CO\\CO}{>}C_{10}H_4(OH)\cdot NH_2.$$

This substance is prepared by heating the foregoing acid with twenty times its weight of nitrobenzene in a reflux apparatus. As the boiling point is approached the liquid becomes dark-red and water separates. By employing only a short air condenser the water escapes, and when it has all disappeared the liquid is filtered. The filtrate on cooling deposits the 1-amino-6-hydroxynaphthacenequinone in beautiful, violet crystals possessing a green metallic lustre. The crystals are collected and freed from nitrobenzene by extracting several times with boiling benzene :

0·1310 gave 0·3572 CO_2 and 0·0479 H_2O. C = 74·37 ; H = 4·07.

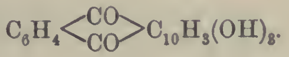
$C_{18}H_{11}O_3N$ requires C = 74·74 ; H = 3·87 per cent.

1-*Amino-6-hydroxynaphthacenequinone* is almost insoluble in aqueous caustic potash, sparingly soluble in alcoholic potash with a red-violet colour. Ordinary organic solvents dissolve it only to a slight extent. It dissolves unchanged in concentrated sulphuric acid with a violet colour ; hot fuming sulphuric acid converts it into a sulphonic acid which dyes chrome- and alum-mordanted wool violet and reddish-violet respectively.

When diazotised in concentrated sulphuric acid and boiled with water, dihydroxynaphthacenequinone is produced, identical with the dihydroxynaphthacenequinone described by Gabriel and Leupold (*Ber.*, 1898, **31**, 1279) and Deichler and Weizmann (*Ber.*, 1903, **36**, 547).

Furthermore, 1-amino-6-hydroxynaphthacenequinone is identical with that prepared by Deichler and Weizmann (*loc. cit.*) and Orchardson and Weizmann (Trans., 1906, **89**, 121).

Trihydroxynaphthacenequinone,



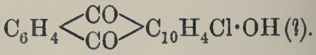
$$C_6H_4{<}\substack{CO\\CO}{>}C_{10}H_3(OH)_3.$$

1-Amino-6-hydroxynaphthacenequinone is best sulphonated by heating it with boric acid (1 part) and fuming sulphuric acid (3 parts of acid containing 60 per cent. of SO_3) in the autoclave to 180—185° for two hours. The product is poured into ice-water and precipitated by the addition of common salt. The crude acid dissolves in water, forming a crimson-red solution with a violet tint. We were unable to isolate the acid in a sufficiently pure state for analysis. When fused with caustic potash, it yields trihydroxynaphthacenequinone. The fusion is carried out in a nickel crucible (1 part of acid, 3½ parts of caustic potash) at 200—250° until the violet colour of the aqueous solution changes to a pure red. The product is dissolved in water, acidified with hydrochloric acid, the brown, flocculent precipitate collected, washed with water, dried, and crystallised from nitrobenzene, from which it separates in deep-brown crystals with a green metallic lustre:

0·1522 gave 0·3934 CO_2 and 0·0405 H_2O. C = 70·5; H = 2·9.

$C_{18}H_{10}O_5$ requires C = 70·6; H = 3·2 per cent.

Trihydroxynaphthacenequinone is very sparingly soluble in organic solvents; it dissolves in concentrated sulphuric acid with a red colour, in aqueous caustic potash with a beautiful pure red shade recalling that of purpurin; the colour fades when the alkaline solution is allowed to stand. It dissolves sparingly in a solution of alum, producing a rose-coloured, fluorescent solution.

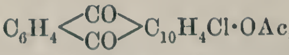
1-*Chloro*-6-*hydroxynaphthacenequinone*,  $C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_{10}H_4Cl\cdot OH$ (?).

As stated in the introduction, 1-hydroxynaphthacenequinone is only attacked by chlorine at a high temperature, and we have found chlorination is conveniently effected in the following manner. 1-Hydroxynaphthacenequinone is loosely packed in a combustion tube, heated in a furnace to a temperature not exceeding 300°, and a current of dry chlorine is passed through the tube. The course of the reaction is easily followed by observing the partial fusion of the product, and when the whole of it is pasty it is removed from the tube and crystallised from nitrobenzene, from which it separates in brown needles, but after further recrystallisation with the aid of animal charcoal it is obtained in pale yellow needles melting at 290—293°:

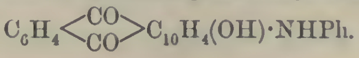
0·1668 gave 0·0794 AgCl. Cl = 11·67.

$C_{18}H_9O_3Cl$ requires Cl = 11·50 per cent.

1-*Chloro*-6-*hydroxynaphthacenequinone* is soluble in hot nitrobenzene or acetic acid, but sparingly so in hot alcohol or benzene. It dissolves in concentrated sulphuric acid with an intense red colour. Aqueous caustic potash scarcely dissolves it, but it is soluble in alcoholic potash with a red colour.

Chloroacetoxynaphthacenequinone,  $C_6H_4\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_{10}H_4Cl\cdot OAc$, results when the foregoing substance is boiled with acetic anhydride and a little zinc chloride until solution is complete. The product is poured into water and the light yellow precipitate collected, washed with water, dried, and crystallised from nitrobenzene or acetic acid, in which latter it is only sparingly soluble. It melts at 270—273° and is hydrolysed by boiling with aqueous caustic potash or concentrated sulphuric acid.

1-*Anilino-6-hydroxynaphthacenequinone*,

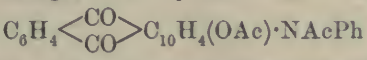


$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_{10}H_4(OH)\cdot NHPh.$$

This derivative is readily produced by boiling chlorohydroxynaphthacenequinone with five times its weight of aniline for an hour. On cooling, and especially on the addition of alcohol, the product separates in beautiful, deep brown crystals with a metallic lustre :

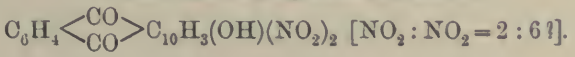
0·1084 gave 0·3131 CO_2 and 0·0430 H_2O. C = 78·77 ; H = 4·33.
0·1862 „ 7·0 c.c. nitrogen at 16° and 764 mm. N = 4·40.
$C_{21}H_{15}O_3N$ requires C = 78·90 ; H = 4·11 ; N = 3·84 per cent.

Anilinohydroxynaphthacenequinone is sparingly soluble in alcohol or acetic acid, readily so in hot aniline or nitrobenzene. Its solution in alcoholic potash is deep blue-violet, and sulphuric acid dissolves it, forming a red solution, which, on heating, becomes reddish-yellow and fluorescent, doubtless owing to the formation of an acridine derivative.

When boiled with acetic anhydride and a little zinc chloride, the colour changes to yellow and *acetanilinoacetoxynaphthacenequinone*,  $C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_{10}H_4(OAc)\cdot NAcPh$ is produced. The product is poured into water, collected, washed with water, dried, and crystallised from acetic acid :

0·1747 gave 0·4756 CO_2 and 0·0655 H_2O. C = 74·3 ; H = 4·17.
0·1371 „ 4·2 c.c. nitrogen at 15° and 736 mm. N = 3·52.
$C_{28}H_{19}O_5N$ requires C = 74·83 ; H = 4·23 ; N = 3·12 per cent.

Dinitrohydroxynaphthacenequinone,



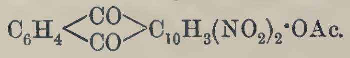
$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_{10}H_3(OH)(NO_2)_2\ [NO_2 : NO_2 = 2 : 6 ?].$$

To prepare this substance, 1-hydroxynaphthacenequinone is dissolved with an equal part of boric acid in concentrated sulphuric acid and treated with an excess of nitric acid, the temperature of the mixture being kept below 5°. The product is poured into water, the precipitate collected, washed with water, dried, and purified by crystallising from nitrobenzene, from which it separates in reddish-brown crystals melting at 275° :

0·1185 gave 0·2538 CO_2 and 0·0310 H_2O. C = 58·17 ; H = 2·90.
0·1198 „ 7·5 c.c. nitrogen at 21·5° and 762 mm. N = 7·13.
$C_{18}H_8O_7N_2$ requires C = 59·34 ; H = 2·17 ; N = 7·69 per cent.

Dinitrohydroxynaphthacenequinone dissolves in warm sulphuric acid with a brownish-yellow colour ; it gives with caustic soda a blue sodium salt which is sparingly soluble in water.

When boiled for a few minutes with acetic anhydride and a little zinc chloride, it yields *dinitroacetoxynaphthacenequinone*,



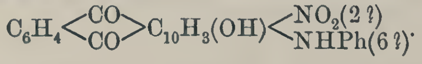
$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_{10}H_3(NO_2)_2\cdot OAc.$$

This is obtained pure by pouring the product into water, collecting the precipitate, washing, drying, and crystallising from acetic acid, from which it separates in yellow crystals melting at 276—278° with effervescence:

0·1026 gave 0·2310 CO_2 and 0·0269 H_2O. C = 58·71; H = 2·83.
0·1206 „ 7·8 c.c. nitrogen at 15° and 756 mm. N = 7·5.
$C_{20}H_{10}O_8N_2$ requires C = 59·11; H = 2·46; N = 6·90 per cent.

It is sparingly soluble in alcohol or benzene. In warm sulphuric acid it dissolves with a yellowish-red colour.

Mononitroanilinohydroxynaphthacenequinone,



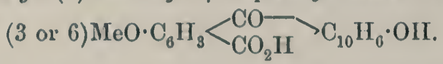
$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_{10}H_3(OH)<\genfrac{}{}{0pt}{}{NO_2(2?)}{NHPh(6?)}.$$

This derivative is obtained by boiling dinitrohydroxynaphthacenequinone with aniline until the red colour of the solution has changed to a bluish-violet. On cooling, it separates in black crystals with a metallic lustre, and is purified by recrystallising from aniline:

0·1322 gave 0·3416 CO_2 and 0·0402 H_2O. C = 70·47; H = 3·38.
0·1819 „ 10·5 c.c. nitrogen at 14° and 754 mm. N = 6·85.
$C_{24}H_{14}O_5N_2$ requires C = 70·24; H = 3·41; N = 6·83 per cent.

Mononitroanilinohydroxynaphthacenequinone dissolves in sulphuric acid with an intense violet colour. It is insoluble in aqueous caustic potash, but dissolves in alcoholic potash, yielding an intense blue solution.

1′-*Hydroxy*-3(6)-*methoxy*-2-β-*naphthoylbenzoic Acid*,



$$(3\text{ or }6)MeO\cdot C_6H_3<\genfrac{}{}{0pt}{}{CO—}{CO_2H}>C_{10}H_6\cdot OH.$$

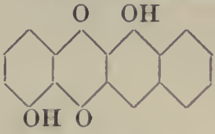
This acid is produced by heating 3-methoxyphthalic anhydride (5 grams) and boric acid (15 grams) in a porcelain dish until partial fusion takes place, then, after finely powdering the mass, mixing with α-naphthol (4 grams) and boric acid (10 grams) and reheating to 190—195° for about an hour. The fused product is poured into water and extracted several times with boiling water to remove boric acid. The residue is boiled with sodium carbonate and animal charcoal, the liquid filtered and acidified with hydrochloric acid, when 1′-hydroxy-3(6)-methoxy-2-β-naphthoylbenzoic acid is precipitated in yellow flocks. This acid is purified by crystallising from alcohol or benzene:

0·1246 gave 0·3238 CO_2 and 0·0510 H_2O. C = 70·88 ; H = 4·55.

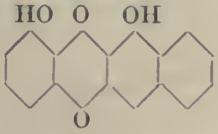
$C_{19}H_{14}O_5$ requires C = 70·81 ; H = 4·35 per cent.

It melts at 210—215° and is readily soluble in acetone or acetic acid.

1 : 7(10)-*Dihydroxynaphthacenequinone*,



or



The acid just described dissolves in concentrated sulphuric acid with a brown colour, which on heating changes to a beautiful reddish-violet. When the intensity of the colour is at its maximum the product is poured into water, the precipitate filtered, washed with sodium carbonate and water, dried, and crystallised from nitrobenzene :

0·1221 gave 0·3320 CO_2 and 0·0426 H_2O. C = 74·16 ; H = 3·88.

$C_{18}H_{10}O_4$ requires C = 74·48 ; H = 3·45.

1 : 7(10)-*Dihydroxynaphthacenequinone* melts indefinitely at 280—300°, and is soluble in concentrated sulphuric acid, forming a reddish-violet, fluorescent solution. It is sparingly soluble in aqueous caustic potash and in hot sodium carbonate solution, but dissolves in alcoholic potash with a red colour. It is also soluble in acetic acid, nitrobenzene, or hot alcohol.

4(5) : 1′-*Dihydroxy-2-β-naphthoylbenzoic Acid.*

The preparation of this acid from 4-hydroxyphthalic acid is carried out in exactly the same manner as that just described in the case of hydroxymethoxynaphthoylbenzoic acid (p. 420). The crude acid is purified by crystallising from alcohol or acetic acid :

0·1183 gave 0·3031 CO_2 and 0·0460 H_2O. C = 69·87 ; H = 4·32.

$C_{18}H_{12}O_5$ requires C = 70·13 ; H = 3·89 per cent.

4(5) : 1′-*Dihydroxy-2-β-naphthoylbenzoic acid* melts at 215—216°, and is soluble in alcohol, benzene, or acetic acid ; it dissolves in alkalis with a yellow colour.

4(5) : 1′-*Dimethoxy-2-β-naphthoylbenzoic Acid.*

When dihydroxynaphthoylbenzoic acid is dissolved in methyl alcohol and shaken with a large excess of dimethyl sulphate and sufficient caustic potash to maintain a slight alkalinity, the methyl ester of 4(5) : 1′-dimethoxy-2-β-naphthoylmethoxybenzoic acid is formed and separates, when the above alcoholic solution is diluted with water, as a heavy oil which slowly solidifies. This ester, when boiled with alcoholic potash and poured into dilute hydrochloric acid, yields the corresponding acid which crystallises from methyl alcohol in colourless needles melting at 195—197°:

0·1704 gave 0·4455 CO_2 and 0·0728 H_2O. C = 71·30; H = 4·75.

$C_{20}H_{16}O_5$ requires C = 71·43; H = 4·76 per cent.

4(5):1′-*Dimethoxy-2-β-naphthoylbenzoic acid* dissolves in alcohol, benzene, or acetic acid; its solution in aqueous sodium carbonate has a faint yellow colour.

1:8(9)-*Dihydroxynaphthacenequinone.*

This substance is prepared by heating dihydroxynaphthoylbenzoic acid with boric acid (1 part) and concentrated sulphuric acid (10 parts) at 140°. The colour becomes intensely red, and when no further change is observed, the product is cooled, poured into water and the precipitate collected, washed with sodium carbonate, then with water, dried, and crystallised from nitrobenzene. It forms yellowish-red needles which do not melt at 330°:

0·1125 gave 0·3070 CO_2 and 0·0377 H_2O. C = 74·4; H = 3·7.

$C_{18}H_{10}O_4$ requires C = 74·48; H = 3·45 per cent.

1:8(9)-*Dihydroxynaphthacenequinone* is soluble in hot nitrobenzene or acetic acid, sparingly so in alcohol or benzene. It gives yellowish-red solutions with aqueous sodium carbonate or caustic potash.

When heated on the water-bath with acetic anhydride and a little zinc chloride it is converted into

1:8(9)-*Diacetoxynaphthacenequinone.*

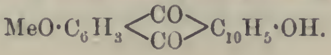
This compound is isolated by precipitation and washing with water, drying, and crystallising from acetic acid, from which it separates in pale yellow needles melting at 227—228°:

0·1320 gave 0·3415 CO_2 and 0·0445 H_2O. C = 70·53; H = 3·71.

$C_{22}H_{14}O_6$ requires C = 70·60; H = 3·74 per cent.

This substance is soluble in alcohol or benzene and dissolves in concentrated sulphuric acid (with hydrolysis), giving a reddish-violet solution; in cold aqueous caustic potash it is insoluble, but when heated it undergoes hydrolysis and dissolves with a yellowish-red colour. On treating with concentrated nitric acid it dissolves, and on dilution with water a crystalline nitro-compound separates.

1-*Hydroxy*-8(9)-*methoxynaphthacenequinone*,



$$MeO\cdot C_6H_3<\begin{matrix}CO\\CO\end{matrix}>C_{10}H_5\cdot OH.$$

When dimethoxynaphthoylbenzoic acid is dissolved with boric acid in sulphuric acid on the water-bath, condensation takes place, the colour becoming reddish-violet. The quinone is isolated and purified in the same manner as dihydroxynaphthacenequinone (p. 422). It forms a crystalline, pale yellow powder melting indefinitely at 250°:

0·1220 gave 0·3347 CO_2 and 0·0476 H_2O. C = 74·82; H = 4·33.

$C_{19}H_{12}O_4$ requires C = 75·00; H = 3·95 per cent.

It is sparingly soluble in hot alcohol, acetic acid, or benzene, soluble in alcoholic potash with a cherry red colour; with aqueous caustic potash it forms an almost insoluble red salt which resembles that of monohydroxynaphthacenequinone. In cold concentrated sulphuric acid it dissolves with a reddish-violet colour, which on heating above 100° changes to red, indicating hydrolysis of the methoxy-group:

4′-*Amino*-1′:4(5)-*dihydroxy*-2-*β*-*naphthoylbenzoic Acid*.

This acid is prepared by combining diazobenzene chloride with dihydroxynaphthoylbenzoic acid and reducing the azo-derivative so formed with stannous chloride and hydrochloric acid. The method of procedure is exactly the same as that given for aminohydroxynaphthoylbenzoic acid (p. 416). It is purified by dissolving in aqueous sodium carbonate and precipitating with hydrochloric acid. It is sparingly soluble in alcohol, benzene, or light petroleum; in sodium carbonate solution it dissolves with a deep yellow colour:

0·1188 gave 0·2909 CO_2 and 0·0457 H_2O. C = 66·78; H = 4·27.

0·1997 ,, 7·3 c.c. nitrogen at 17° and 770 mm. N = 4·37.

$C_{18}H_{13}O_5N$ requires C = 66·87; H = 4·04; N = 4·33 per cent.

When heated alone or in acetic acid or nitrobenzene this acid undergoes condensation, with the elimination of water and formation of

1-*Amino*-6:8(9)-*dihydroxynaphthacenequinone*.

The method of preparation of this substance is exactly similar to that described in the case of (1)-amino-6-hydroxynaphthacenequinone (p. 417).

This *aminodihydroxynaphthacenequinone* dissolves in cold sulphuric acid with an intense bluish-red colour and in alcoholic potash with a reddish-blue colour. It is readily oxidised by potassium dichromate in acetic acid solution:

0·1185 gave 0·3058 CO_2 and 0·0427 H_2O. C = 70·37 ; H = 4·0.
0·1673 „ 7·2 c.c. nitrogen at 15° and 744 mm. N = 5·01.
$C_{18}H_{11}O_4N$ requires C = 70·8 ; H = 3·6 ; N = 4·6 per cent.

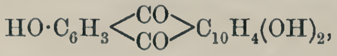
6′ (?)-*Bromo*-1′ : 4(5)-*dihydroxy*-2-*β*-*naphthoylbenzoic Acid.*

This derivative is obtained when an excess of bromine is added to dihydroxynaphthoylbenzoic acid suspended in carbon disulphide and the mixture gently warmed on the water-bath for two hours. The carbon disulphide and the excess of bromine are then allowed to evaporate spontaneously and the solid residue crystallised from acetic acid, from which it separates in needles melting at 270° with decomposition :

0·1467 gave 0·2996 CO_2 and 0·0403 H_2O. C = 55·70 ; H = 3·05.
0·1888 „ 0·0938 AgBr. Br = 21·13.
$C_{18}H_{11}O_5Br$ requires C = 55·81 ; H = 2·84 ; Br = 20·67 per cent.

This acid is sparingly soluble in alcohol or benzene, readily so in hot acetic acid. It dissolves in sodium carbonate with a deep yellow colour.

When heated with boric acid in concentrated sulphuric acid to 180° condensation occurs and at the same time hydrogen bromide and bromine are evolved and a *trihydroxynaphthacenequinone*,



$$HO\cdot C_6H_3<\begin{array}{c}CO\\ CO\end{array}>C_{10}H_4(OH)_2,$$

is produced. This quinone was isolated and purified in the usual manner and obtained as a brown, crystalline powder. We were, however, unable to obtain it quite pure, as even after several recrystallisations it still contained traces of bromine.

1′ : 5′-*Dihydroxy*-2-*β*-*naphthoylbenzoic Acid.*

This acid is best prepared in the following manner.

Phthalic anhydride (20 grams) and boric acid (50 grams) are partly fused in a porcelain basin, then powdered and mixed with 1 : 5-dihydroxynaphthalene (20 grams) and heated to 200° for three hours. The product is extracted with boiling water until free from boric acid and the residue boiled with sodium carbonate, filtered, and acidified with hydrochloric acid. The brown, resinous precipitate is collected, boiled with water and calcium carbonate, the solution of the calcium salt filtered, and the acid reprecipitated by the addition of hydrochloric acid. The precipitated acid is collected and purified by crystallising from acetic acid :

0·1069 gave 0·2732 CO_2 and 0·0395 H_2O. C = 69·70 ; H = 4·11.
$C_{18}H_{12}O_5$ requires C = 70·13 ; H = 3·89 per cent.

1′ : 5′-*Dihydroxy*-2-*β*-*naphthoylbenzoic acid* melts at 221° and is soluble in alcohol, acetone, or acetic acid. In sodium carbonate solution it dissolves with a deep yellow colour.

1′ : 5′-*Dimethoxy-2-β-naphthoylbenzoic Acid.*—When the acid just described is dissolved in alcohol and shaken at 20—25° with excess of dimethyl sulphate and sufficient aqueous caustic potash to render the solution distinctly alkaline, the methyl ester of dimethoxynaphthoylbenzoic acid is obtained, on dilution with water, as an oil which gradually crystallises. This oil, when boiled with alcoholic potash and poured into dilute hydrochloric acid, yields dimethoxynaphthoylbenzoic acid as a white precipitate, which is collected and purified by crystallising from acetic acid :

0·1810 gave 0·4737 CO_2 and 0·0780 H_2O. C = 71·38 ; H = 4·79.

$C_{20}H_{16}O_5$ requires C = 71·4 ; H = 4·8 per cent.

1′ : 5′-*Dimethoxy-2-β-naphthoylbenzoic acid* melts at 209—210°, and dissolves in alkalis with a pale yellow colour. It dissolves in cold concentrated sulphuric acid with a brown colour, which on heating changes to green, indicating the formation of

5 : 1-*Hydroxy-5-methoxynaphthacenequinone.*

This quinone is isolated from the green sulphuric acid solution by precipitating with water, collecting, drying, and crystallising from nitrobenzene :

0·1960 gave 0·5383 CO_2 and 0·0704 H_2O. C = 74·91 ; H = 3·99.

$C_{19}H_{12}O_4$ requires C = 75·0 ; H = 3·9 per cent.

1-*Hydroxy-5-methoxynaphthacenequinone* crystallises in red needles, and dissolves in alcoholic potash with a red, in concentrated sulphuric acid with a green, colour. The latter changes on heating to blue, owing to the hydrolysis of the methoxy-group. The quinone is soluble in acetic acid or nitrobenzene, sparingly so in alcohol or benzene.

1 : 5-*Dihydroxynaphthacenequinone-4?-sulphonic Acid.*

1′ : 5′-Dimethoxy-2-β-naphthoylbenzoic acid differs from the corresponding dihydroxy-acid in its behaviour when warmed with boric and sulphuric acids. The dimethoxy-acid is condensed to the quinone without sulphonation, but the dihydroxy-acid yields 1 : 5-dihydroxynaphthacenequinonesulphonic acid, which is precipitated on dilution with water. Purified by crystallising from dilute alcohol, it is obtained as a red, crystalline powder :

0·1028 gave 0·2277 CO_2 and 0·0397 H_2O. C = 60·41 ; H = 4·29.
0·1805 ,, 0·1092 $BaSO_4$. S = 8·31.

$C_{18}H_{10}O_7S$ requires C = 58·38 ; H = 2·70 ; S = 8·65 per cent.

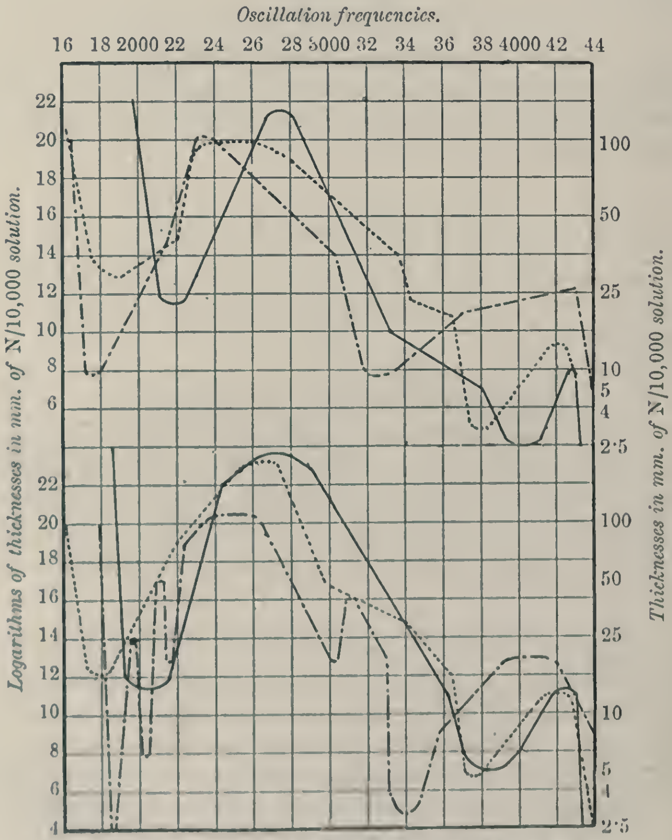
The acid dissolves in alkalis and in sulphuric acid with a violet-blue colour. It is soluble in water, sparingly so in alcohol. It dyes wool a reddish-yellow shade, and has some affinity for cotton.

THE UNIVERSITY,
MANCHESTER.

Addendum by E. C. C. BALY and W. B. TUCK.

The absorption curves of these compounds are shown in Figs. 1—15, the full curve in each case being that obtained with a solution of the compound in alcohol, the dotted curve being obtained after the addition of excess of sodium ethoxide, whilst the dot and dash curve is

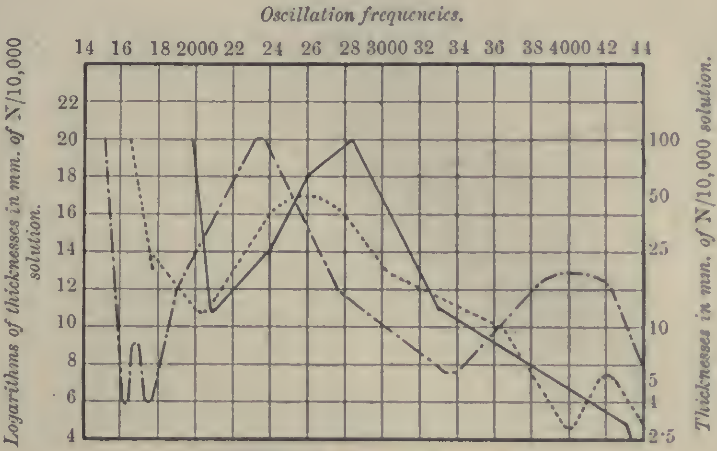
FIGS. 1 and 2.



Upper curves *monohydroxynaphthacenequinone.*
Lower ,, *1 : 6-dihydroxynaphthacenequinone.*

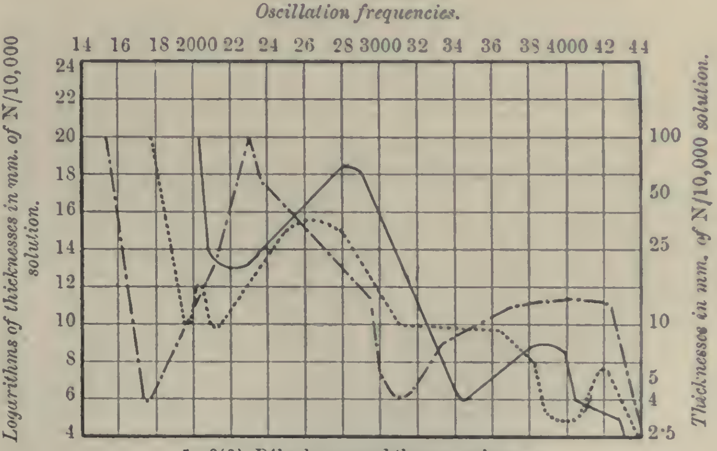
that obtained with a solution in concentrated sulphuric acid containing about 3 per cent. of boric acid. In each case $N/10,000$ solutions were employed and the curves drawn by plotting the logarithms of the thicknesses of the solution used against the limits of absorption.

FIG. 3.



1 : 7(10)-*Dihydroxynaphthacenequinone.*

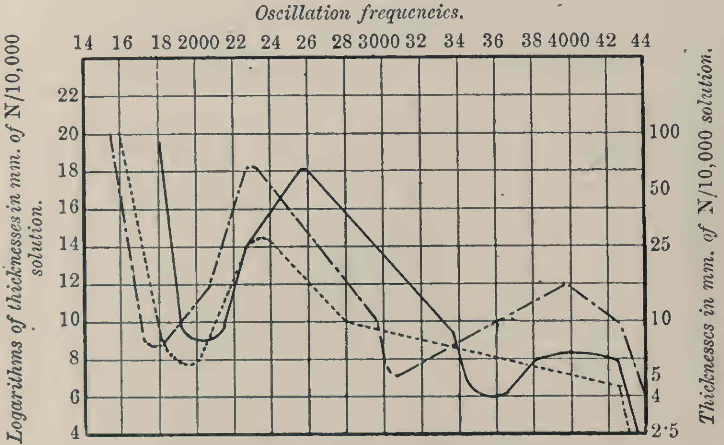
FIG. 4.



1 : 8(9)-*Dihydroxynaphthacenequinone.*

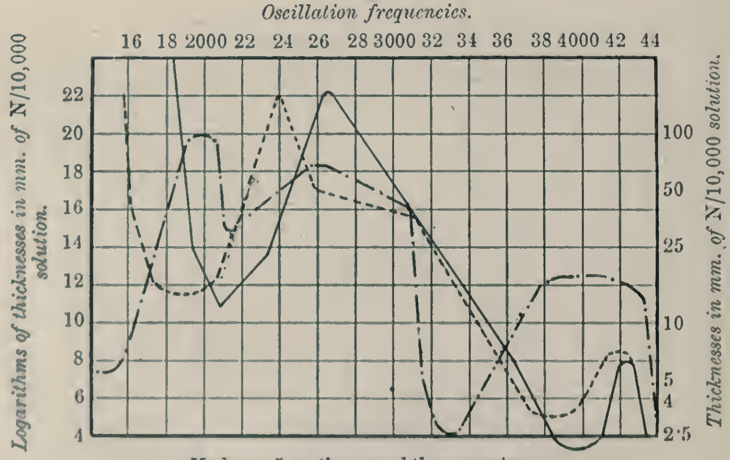
In Fig. 1 are shown the three curves of 1-hydroxynaphthacenequinone, which establish the type of absorption exhibited by all the compounds described in the paper; the full and dotted curves, representing the absorption of 1-hydroxynaphthacenequinone in neutral and alkaline alcoholic solutions respectively, show the existence of two absorption bands, one in the ultra-violet due to the presence of a certain amount of benzenoid tautomerism and the other, due to isorropesis, in the visible part of the spectrum. It will be noticed that in Fig. 1, and indeed in all the substances examined, the latter absorption band is nearer to the red when the solution is alkaline. This fact, coupled

FIG. 5.



1 : 2 : 6-*Trihydroxynaphthacenequinone.*

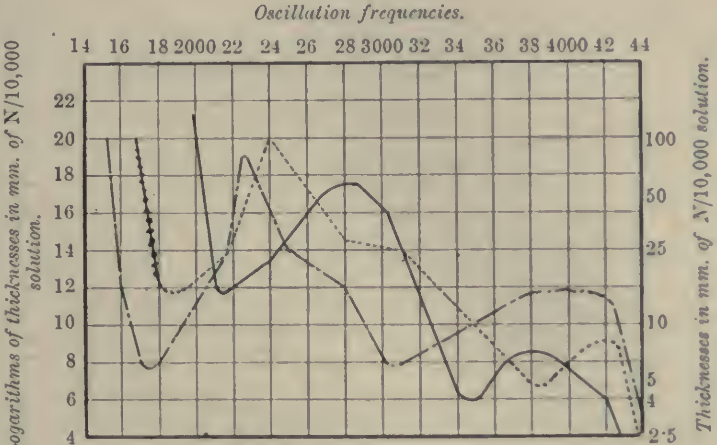
FIG. 6.



Hydroxy-5-methoxynaphthacenequinone.

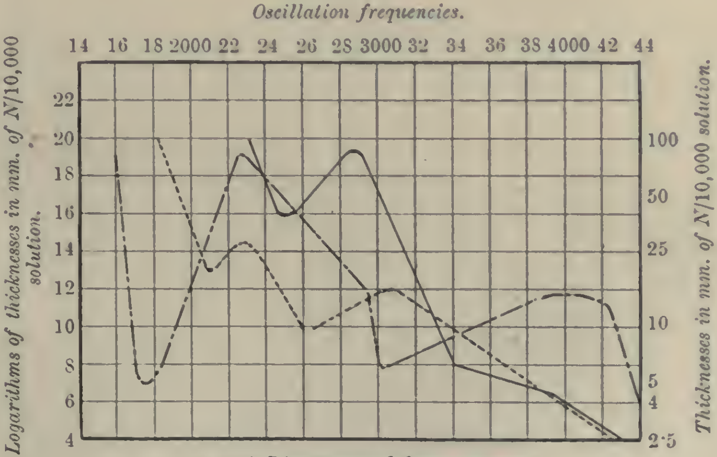
with the fact that the diacetoxynaphthacenequinone (Fig. 8) exhibits only very short absorption bands, shows the isorropesis is not simply one of a quinonoid type between the two carbonyl groups; it is manifest that the process of isorropesis is in some way connected with the presence of the hydroxyl groups in close proximity to the carbonyl groups. It has been pointed out (Baly and Ewbank, Trans., 1905,

FIG. 7.



1-*Hydroxy*-8(9)-*methoxynapthacenequinone.*

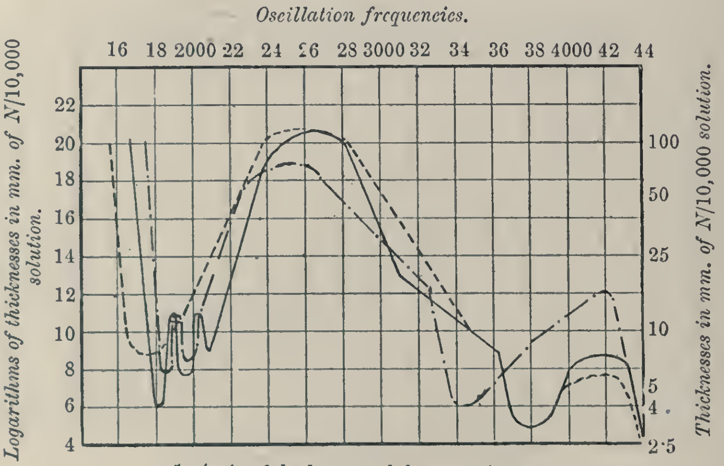
FIG. 8.



1 : 8(9)-*Diacetoxynaphthacenequinone.*

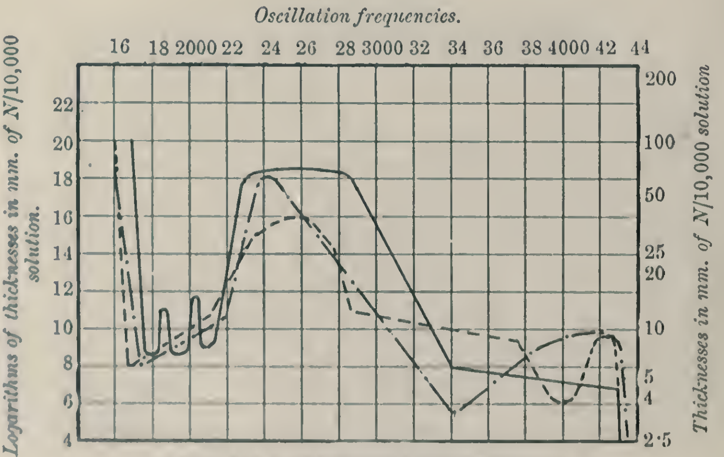
87, 1347) that the absorption band of the phenols is shifted towards the red in alkaline solution, this being also true for the aminophenols; it is probable that in this fact is to be found the explanation of the shift of the isorropesis band of the naphthacenequinone derivatives in alkaline solution, for this band is no doubt due in some way to the phenolic groupings, and any change of frequency in the absorption band

FIG. 9.



1-*Amino*-6-*hydroxynaphthacenequinone.*

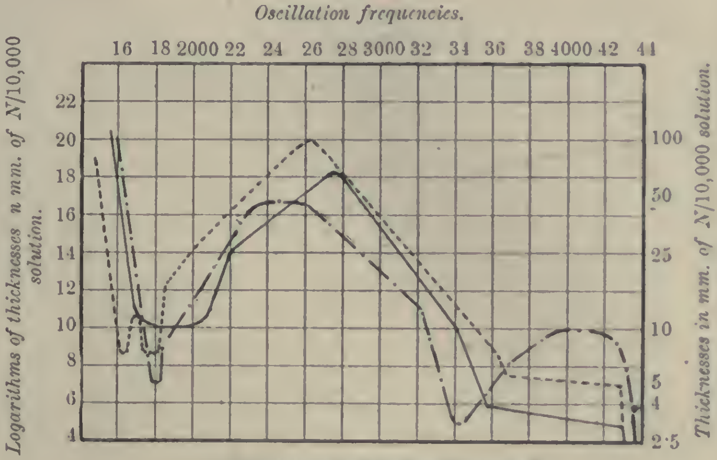
FIG. 10.



1-*Amino*-6:8(9)-*dihydroxynaphthacenequinone.*

produced by the action of alkali on the latter will produce a *pro rata* change in the former.

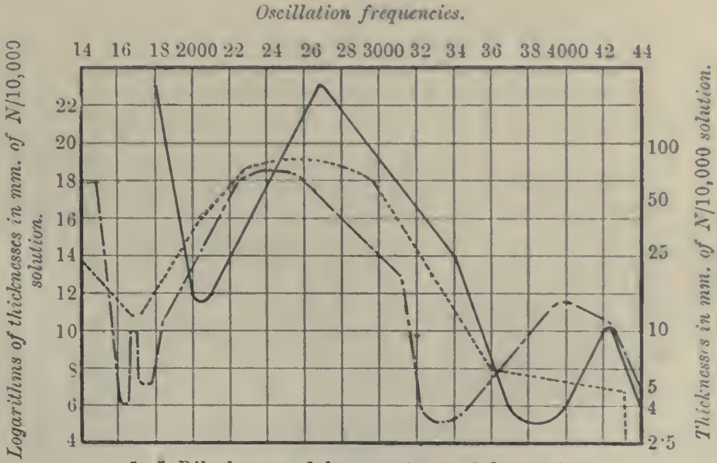
FIG. 11.



1-*Anilino-6-hydroxynaphthacenequinone.*

The absorption spectra show very clearly the different effect obtained by substitution of hydroxyl groups in the naphthalene and the benzene nuclei. The following table shows the position of the heads of the absorption bands and their relative persistence. By the persistence of an absorption band is meant the relative change of

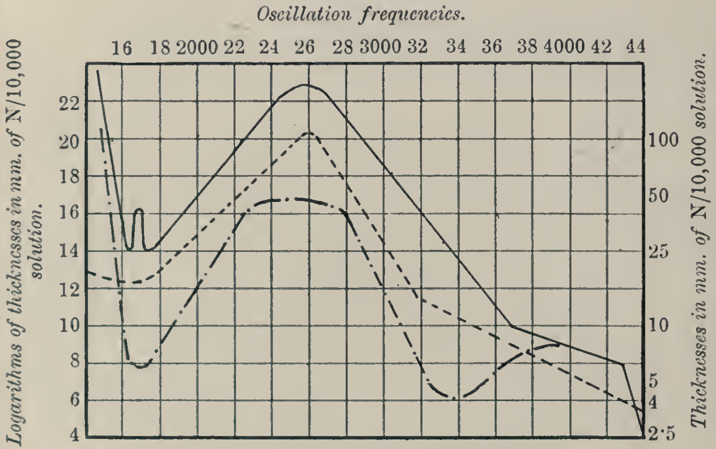
FIG. 12.



1 : 5-*Dihydroxynaphthacenequinonesulphonic Acid.*

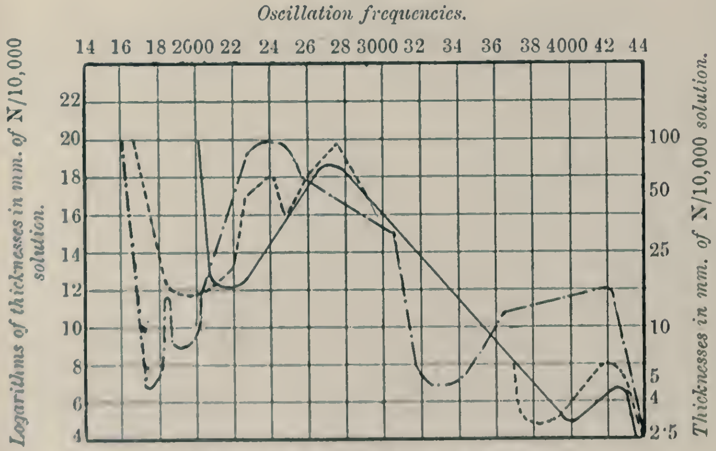
dilution over which the band persists, and this value may be taken as a measure of the process taking place which gives rise to the absorption. The persistence of each band is measured by the distance it extends over the ordinates on the diagrams.

FIG. 13.



2-*Nitro*-6-*anilino*-1-*hydroxynaphthacenequinone.*

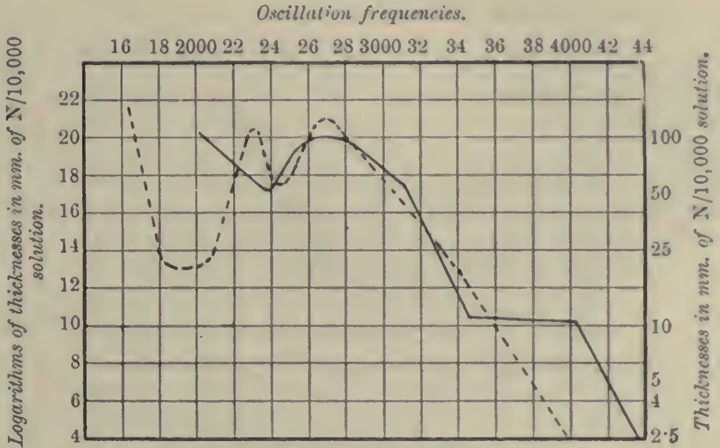
FIG. 14.



1-*Chloro*-6-*hydroxynaphthacenequinone.*

Comparing monohydroxynaphthacenequinone with the 1 : 6-dihydroxy-derivative in which both hydroxyl groups are in the naphthalene residue, it will be seen that in neutral solutions the head of the band has shifted from 2200 to 2050 and in alkaline solution from 1900 to 1800, whilst the persistence has increased from 5 to 6 in the one case and from 3·5 to 5·5 in the other. It is thus evident that the introduction of a second hydroxyl in position 6 both shifts the absorption towards the red and at the same time materially increases the amount of the isorropesis. On the other hand, the introduction of a second hydroxyl group in the benzene residue has the opposite effect; in neutral solution the absorption band is shifted a very little to the red, but in alkaline solution the band is shifted towards the blue. In both the 1 : 7- and the 1 : 8-dihydroxy-compounds the persistence is less than in the monohydroxy-compound; especially is this the case in the 1 : 8-compound. That this phenomenon is not peculiar to the benzene residue is shown by the trihydroxy-compound (1 : 2 : 6 ?), where the absorption band in both alkaline and neutral solution is nearer the blue, and the persistence less than in the monohydroxy-compound, proving that the third hydroxyl group more than counteracts the influence of the second, making the compound less coloured than the monohydroxy-compound.

FIG. 15.



1-*Hydroxy*-2 : 6(?)-*dinitronaphthacenequinone.*

In Figs. 6 and 7 are shown the curves of the 1-hydroxy-5- and -8-methoxy-compounds, and in Fig. 8 those of the 1 : 8-diacetoxy-compound, which show the great effect produced by acetylating the two free hydroxyl groups.

The relative position of the amino- and hydroxyl-groups has very much the same effect as that just ascribed to the hydroxyl groups alone. The following table gives the measurements from the absorption curves of the three aminohydroxy-derivatives described in the paper. It will be noticed that the isorropesis bands tend to subdivide at the heads into two or three narrow bands; this, however, does not influence the measurements, which are purely comparative:

TABLE I.

Compound.	Solvent.	Head of band in oscillation frequencies.	Persistence.
Monohydroxynaphthacenequinone	Alcohol	2200	5
	Alkali	1900	3·5
	Sulphuric acid	1750	6
1 : 6-Dihydroxynaphthacenequinone.........	Alcohol	2050	6
	Alkali	1800	5·5
	Sulphuric acid	1850 2030 2160	(maximum) 8
1 : 7-Dihydroxynaphthacenequinone.........	Alcohol	2100	4·5
	Alkali	2050	3
	Sulphuric acid	1630 1750	7
1 : 8-Dihydroxynaphthacenequinone.........	Alcohol	2200	2·5
	Alkali	1970 2120	3
	Sulphuric acid	1750	7
1 : 2 : 6(?)-Trihydroxynaphthacenequinone.	Alcohol	2050	4·5
	Alkali	1950	3·5
	Sulphuric acid	1750	4·5

TABLE II.

Compound.	Solvent.	Head of bands.	Persistence.
1-Amino-6-hydroxynaphthacenequinone	Alcohol	1800 1960 2080	7·5
	Alkali	1780	6
	Sulphuric acid	1850 1970	5·5
1-Amino-6 : 8-dihydroxynaphthacenequinone	Alcohol	1800 1950 2100	5
	Alkali	1700	4
	Sulphuric acid	1750	5
1-Anilino-6-hydroxynaphthacenequinone	Alcohol	1900	4
	Alkali	1630 1760	5·5
	Sulphuric acid	1800	5

The introduction of the second hydroxyl group in position 8, although it does not materially alter the position of the bands, very considerably decreases the persistence; the same is true when the hydrogen of the amino-group is replaced by the electro-negative phenyl group.

The influence of methylating the hydroxyl groups is shown by the curves in Figs. 6 and 7, whilst the curves obtained with the 1:5-dihydroxysulphonic acid compound are shown in Fig. 12. In Figs. 13—15 the effect of the substitution by chlorine and by the nitro-group is shown. The influence of this substitution is very considerably to reduce the persistence of the bands; the 1-hydroxy-2:6-dinitro-compound was found to be so slightly soluble in sulphuric acid as to render the observation of its absorption impossible in this solvent.

SPECTROSCOPIC LABORATORY,
UNIVERSITY COLLEGE, LONDON.

XLIII.—*Constituents of Natural Indigo.** *Part II.*

By ARTHUR GEORGE PERKIN.

THE first application of the term "Indigo-yellow" to a substance existing in natural indigos is due to Bolley and Crinsoz (*Jahresb.*, 1866, 573), who state that it is to be found in the Bengal variety, and can be isolated by sublimation. It is described as consisting of golden-yellow needles, subliming at 130°, sparingly soluble in water, but dissolved by soda lye. A reference to the existence of a yellow colouring matter in the *Polygonum tinctorium*, an indigo-yielding plant, by Henry (*Gmelin's Handbook of Chemistry*, 1846, xiii, 50), is interesting, and he mentions that this is obtained by treating the dried aqueous extract of the plant with ether.

More recently, Rawson (*J. Soc. Chem. Ind.*, 1899, **18**, 251) observed that Java indigos contained a peculiar compound present usually to the extent of 2 to 3 per cent., but in one special sample as much as about 20 per cent. was found to exist. This substance was soluble in alkalis, with a deep yellow colour; on heating it partially sublimed, and had the properties of an adjective dye-stuff, the shades given with a chromium mordant being similar to those given by vine-leaves or weld. It could readily be detected by adding to the ground indigo a solution of an alkaline hydroxide or ammonia. Rawson considered it quite possible that this yellow substance was derived from the *Indigofera arrecta*, though it might perhaps originate from some other plant accidentally growing with the indigo or purposely added to the vats. Ultimately he ascertained that the former surmise was correct.

Bergtheil (*Report of the Indigo Station, Sirsiah, Calcutta*, 1906) states, "A very small quantity of the yellow colouring matter described by Rawson was present in nearly all indigos made at Pusa,* and has been characteristic of most of the indigos made from it in Bihar this year (p. 15). Further, there is no doubt that manufacturing with immature plant tends to produce this yellow matter" (p. 15).

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* A preliminary account of some of this work has been given in Proc., 1904, **20**, 172 and *ibid.*, 1906, **22**, 199,

EXPERIMENTAL.

Some years ago attempts were made to reproduce the indigo-yellow of Bolley and Crinsoz, but it was found that on subliming samples of the best Bengal indigos, containing as was considered at the time about 75 per cent. of indigotin, no sublimate of this character was obtained, and moreover experiments have failed to detect the presence of such a substance in the indigos themselves. On submitting, however, refined Bengal indigo, stated to contain 92 per cent. of indigotin, to sublimation with limited access of air, a small quantity of a most interesting yellow compound, $C_{15}H_8O_2N_2$, was produced. A preliminary account of these experiments has been published (Proc., 1906, **22**, 198), but this, at first suspected to be Bolley and Crinsoz's indigo-yellow, was not identical with their product, because, not only was it insoluble in alkaline solutions, but it could be heated to 160° without appreciable loss. The appearance of Mr. Rawson's interesting communication again brought the subject to mind, and on application to him he kindly forwarded a small sample of Java indigo containing his yellow compound. This, which weighed approximately 3 grams, could not be distinguished in appearance from an ordinary commercial indigo, but gave with dilute alkalis a deep yellow extract.

To identify, if possible, this substance, the indigo was extracted with boiling alcohol, and the resulting green coloured solution evaporated and poured into ether. The ethereal liquid was well washed with water, filtered, and the ether removed by distillation. The yellow residue was crystallised first from dilute alcohol and finally from acetic acid:

0·1018 gave 0·2350 CO_2 and 0·0360 H_2O. C = 62·95; H = 3·92.
$C_{15}H_{10}O_6$ requires C = 62·93; H = 3·49 per cent.

It formed glistening, yellow needles melting at 276—277°, and dissolved in alkaline solutions with a pale yellow coloration.

The *acetyl* compound crystallised from alcohol in colourless needles melting at 181—182°:

0·1081 gave 0·2410 CO_2 and 0·0425 H_2O. C = 60·82; H = 4·36.
$C_{23}H_{18}O_{10}$ requires C = 60·79; H = 3·96 per cent.

This substance, after crystallisation from methyl alcohol, commenced to melt at about 116°, became fluid at 120°, but on further heating gradually solidified, and finally melted at 181—182°. This behaviour, it has been previously pointed out (Trans., 1902, **81**, 587; *ibid*., 475), is characteristic of acetylkaempferol, and there could be little doubt that the colouring matter in question therefore consisted of kaempferol. An examination of its dyeing and other properties fully corroborated this view.

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* From *Indigofera arrecta*.

The amount of kaempferol present in this sample of indigo was unfortunately not determined accurately, but as much as 0·6 gram was certainly obtained from it. It was now interesting to examine other samples of Java indigo in this respect, and through the kindness of Prof. van Romburgh, of Utrecht, numerous samples were obtained by purchase from Holland. The exact manner by which indigo has been manufactured in Java has been kept secret, except in so far that hot water and sulphuric acid are usually employed, but on the other hand it is known that three distinct methods have been or are in vogue, and may be described as the "new process with hot water," "the new process with cold water," and "the old process in which no chemicals are used." An investigation of samples of the dye-stuff which had been prepared in these three different ways by extraction with alcohol or carbonate of soda solution revealed in each case the presence of kaempferol, but only in minute quantity, for the largest amount that could be isolated was approximately 0·2 per cent. It appears, therefore, that Rawson's indigo was abnormal in containing such a large amount of yellow colouring matter, as in fact he indicates, and it is also probable that by recent improvements in manufacture the Dutch chemists have been successful in preventing the contamination of their indigos with this impurity.

The Glucoside.—As there was some doubt as to the occurrence of kaempferol or its glucoside in the *Indigofera arrecta*, the plant from which this indigo is derived, it was investigated in this respect. The material employed consisted of the air-dried leaves of the Natal plant which had been grown in India, and it should be noted that there is no botanical difference between the Natal and Java varieties, for the *Indigofera arrecta*, originally native of Natal, was introduced into Java from there. For a liberal supply of this I am indebted to the kindness of Mr. W. P. Bloxam.

The leaves were extracted with ten times their weight of boiling water for six hours, the solution evaporated to dryness, the residue incorporated with sand, and digested with boiling alcohol. The alcoholic liquid was concentrated, treated with water, and the mixture evaporated to a small bulk and filtered. The filtrate, on standing several days, slowly deposited crystals, which were collected, washed with chloroform, and recrystallised two or three times from water and finally from dilute alcohol. Analyses of the substance dried at 160° gave the following result:

0·1127 gave 0·2320 CO_2 and 0·0547 H_2O. C = 56·14; H = 5·39.
0·1117 „ 0·2294 CO_2 „ 0·0530 H_2O. C = 56·00; H = 5·27.
$C_{27}H_{30}O_{14}$ requires C = 56·06; H = 5·19 per cent.

When air-dried, the glucoside has the formula $C_{27}H_{30}O_{14},3\frac{1}{2}H_2O$ (H_2O = 9·83 per cent.), which is evolved by heating to 100° (found H_2O = 9·65, 9·68 per cent.), but is again absorbed by standing for some hours in a moist atmosphere.

This substance, for which the name *kaempferitrin* is proposed, consists of a glistening mass of almost colourless needles, which when heated congeal together at 190—192° and melt at 201—203°. It is somewhat sparingly soluble in boiling water and in cold alcohol, and its solution is coloured pale yellow by alkalis. Aqueous lead acetate gives no precipitate, but with basic lead acetate a bright yellow deposit is formed. Ferric chloride produces a greenish-brown coloration.

The hydrolysis of this glucoside was studied quantitatively, employing in each of the cases given below 200 c.c. of water and 2 c.c. of sulphuric acid. After boiling for a short time, the clear liquid commenced to deposit pale yellow crystals, and when the digestion had continued for an hour, the mixture was allowed to stand over night. The product was dried at 160°:

0·6785 gave 0·3300 yellow colouring matter. Found 48·63 per cent.
0·6125 „ 0·3013 „ „ „ „ 49·19 „

The acid liquid from which this substance had been deposited was neutralised with barium carbonate, filtered, and the filtrate evaporated to a small bulk. The residue yielded an osazone, and this, after washing with chloroform and recrystallisation from dilute alcohol, was obtained in yellow needles which melted sharply at 180—182° and had the properties of rhamnose osazone.

The insoluble product of the hydrolysis, which on examination was found to be quite homogeneous, melted at 275—277°, and gave, when dried at 160°, C = 63·01; H = 3·68 per cent.

The acetyl compound, after crystallisation from methyl alcohol, exhibited on heating the peculiar properties of acetylkaempferol, and on analysis gave C = 60·77; H = 4·43 per cent.

On hydrolysis, therefore, kaempferitrin yields kaempferol and rhamnose, and this may be expressed by the equation:

$$C_{27}H_{30}O_{14} + 4H_2O = C_{15}H_{10}O_6 + 2C_6H_{14}O_6.$$

The reaction requires a yield of 49·48 per cent. of kaempferol, and this is in agreement with that actually obtained and given above.

It has been previously shown that robinin (Trans., 1902, 81, 473) is a glucoside of kaempferol, and this in general appearance and melting point somewhat closely resembles kaempferitrin. Again, both glucosides are almost devoid of tinctorial property, although the extremely feeble effects given in the usual manner with mordanted woollen cloth are practically identical in each case. On the other hand, robinin on hydrolysis gives kaempferol, two molecules of rhamnose and one of glucose (?) according to the equation:

$$C_{33}H_{42}O_{20} + 4H_2O = C_{15}H_{10}O_6 + 2C_6H_{14}O_6 + C_6H_{12}O_6,$$

and for this reaction but 37·73 per cent. of kaempferol is required. There can be no doubt, therefore, that robinin and kaempferitrin are distinct substances. The amount of kaempferitrin obtained from the leaf by the above described method was approximately 0·6 per cent. (1·5 grams pure glucoside from 250 grams of leaf). An examination, however, of the mother liquid from which it had been deposited indicated that a considerable quantity still remained dissolved, for although this could not be isolated by the methods employed, its presence was evidenced by the fact that when boiled with dilute sulphuric acid kaempferol was obtained.

It was, however, possible to ascertain how much kaempferol could be produced from the leaf, and for this purpose an extract of 200 grams of the material in 2500 c.c. of water was treated with 10 c.c. of sulphuric acid and digested at the boiling point for one hour. On cooling overnight a claret-red coloured precipitate had separated, and this was collected, dissolved in a little alcohol and poured into a large volume of ether. The claret-red impurity being insoluble in the ether was thus removed, and the clear liquid containing the kaempferol was then washed with water and evaporated to dryness.

The residue, after extraction with water, was dried, and then consisted of a yellowish-pink, crystalline mass which weighed 3·956 grams. Thus the air-dried leaf gave approximately 2 per cent. of kaempferol, and would accordingly contain about 4 per cent. of glucoside on the assumption, as is probable, that this consists entirely of kaempferitrin.

From the experiments of Rawson (*Report on the Cultivation and Manufacture of Indigo, Muzufferpore*, 1904), it is probable that the quantity of kaempferol which the leaf is capable of yielding varies with the season of the year, for although no direct estimations of the yellow colouring matter actually given by the plant appear to have been made, the amount present in the indigo produced from it is suggestive. Thus indigo prepared from the young leaves contained much yellow dye, whereas in the old leaf product it was absent.

An examination was now made of the leaves of the ordinary Indian plant, *I. Sumatrana*, with the result that these were also found to contain a trace of a yellow colouring matter. The amount present was very minute, however, and from 2 kilos. of the leaves insufficient was isolated for its satisfactory characterisation. Its dyeing properties were very similar to those given by kaempferol, so that it possibly consists of this substance.

This result seems to indicate that Bolley and Crinsoz's indigo-yellow (*loc. cit.*) cannot be identical with kaempferol. On the other hand, as Bengal indigos do not appear to give a yellow sublimate of the character they describe, it is possible that they were mistaken as to the source of the material they employed. It was ascertained that if indigo mixed with 10 per cent. of kaempferol is cautiously sublimed between watch glasses, the sublimate produced contains appreciable quantities of the yellow colouring matter.

The hydrolysis of the kaempferitrin which exists in the leaf during the process of indigo manufacture may possibly be due to the presence of a specific enzyme, although at present preliminary experiments in this direction have been unsuccessful. The subject of the indigo enzyme has recently been discussed by Orchardson, Wood and Bloxam (*J. Soc. Chem. Ind.*, 1907, **26**, 4), whose results with the air-dried leaf are in harmony with those of the Dutch chemists who describe an insoluble enzyme, rather than with those of Bergtheil, who considers this to be soluble in water. A study of the behaviour of the insoluble preparation, and of one which had been very kindly forwarded to this laboratory by Prof. Beyerinck of Delft, both of which readily hydrolysed indican, was made at varied temperatures on solutions of kaempferitrin with negative result.

Apart, however, from the question of enzyme hydrolysis, it is likely that the use of sulphuric acid when manufacturing indigo from the Java plant may result in the contamination of the dye-stuff with kaempferol. In this case the wet indigo sludge or "mal" is boiled with a little sulphuric acid, and as a result any kaempferitrin present in the adhering water would naturally be transformed into the insoluble colouring matter and remain with the indigo. If it is considered that the fresh leaf will yield but 1 per cent. of indigotin, and that it may also contain 1 per cent. of the kaempferol glucoside, the presence of but 2 to 3 per cent. of the yellow colouring matter in the finished indigo cake seems quite easy of explanation in this way.

The author is indebted to the Research Fund Committee of the Chemical Society for a grant which has been in part employed to cover the expenses of this research.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY,
LEEDS.

XLIV.—*Association of Phenols in the Liquid Condition.*

By JOHN THEODORE HEWITT and THOMAS FIELD WINMILL.

IT is a well recognised fact that substances containing hydroxyl groups usually form associated molecules when in the liquid condition, the results obtained in this direction being mainly due to the researches of Ramsay and his co-workers (Ramsay and Shields, *Phil. Trans.*, 1893, **184**, 655; Trans., 1893, **63**, 1089; Aston and Ramsay, Trans., 1894, **65**, 167; *Zeitsch. physikal. Chem.*, 1893, **12**, 433; 1894, **15**, 89; Ramsay, *ibid.*, **15**, 106).—These authors applied a method indicated by Eötvös (*Wied. Annalen*, 1886, **27**, 452), and although the method of calculation employed has been fully explained in the papers quoted, a short reference seems desirable here, as the original expression was subsequently modified.

The assumption made by Ramsay and Shields in their first paper was that

$$K = \frac{d[\gamma(Mv)^{\frac{2}{3}}]}{dt}$$

should be the same for different liquids when γ is the surface tension, M the molecular weight of substance, v the specific volume, and t the temperature. This expression holds for substances which are non-associated in the liquid state, and a large number of compounds gave a mean value of this coefficient equal to 2·121. This number is not appreciably exceeded except in particular cases where experimental errors are likely to arise. A lower value is, however, frequently found and in such cases the molecular complexity may be deduced. For if K' be the coefficient found experimentally, the assumed molecular weight, M, in the calculation should be multiplied by

$$\left(\frac{2{\cdot}121}{K'}\right)^{\frac{3}{2}} = x$$

in order to obtain the mean molecular weight of the liquid. The quantity x was at first described as the factor of association, but has since been shown to be probably greater than the average complexity. Van der Waals (*Zeitsch. physikal. Chem.*, 1894, **13**, 657) substituted the expression

$$x^{\frac{2}{3}} = \frac{k(\tau' - \tau) + \sigma'_M}{\sigma_M}$$

for that given by Ramsay; whilst Ramsay (*Proc. Roy. Soc.*, 1894, **56**, 175, and *Zeitsch. physikal. Chem.*, 1894, **15**, 112), finding that the values for the molecular surface energy are generally well satisfied by the expressions of the form

$$\gamma(Mv)^{\frac{2}{3}} = \frac{k(\tau - d)}{1 + \mu\tau},$$

where τ is the temperature expressed in degrees below the critical point, deduces the equation

$$x = \left[\frac{2{\cdot}121}{k}(1 + \mu\tau)\right]^{\frac{3}{2}}$$

for calculating the factor of association. The effect of these corrections, is shown in the annexed table:

Substance.	Ramsay and Shields (uncorrected).	Van der Waals (corrected).	Ramsay (corrected).
Water	3·8 (0—10°)	1·9 (0°)	1·707 (0°)
Methyl alcohol ...	3·43 (16—46)	2·1 (20)	2·32 (20)
Ethyl ,, ...	2·74 (16—46)	1·61 (20)	1·65 (20)
Acetic acid	3·62 (16—46)	—	2·13 (20)

Subsequent workers who have used this method for the determination of molecular complexity have simply used the uncorrected expression: reference may be made to the papers of Bottomley (who points out that his results on account of being uncorrected are probably too high, Trans., 1903, **83**, 1421) on the molecular formulæ of fused salts and of G. Carrara and G. Ferrari (*Gazzetta*, 1906, **36**, 419) on the complexity of various aliphatic compounds.

Amongst the hydroxylic compounds examined by Ramsay and Shields (*loc. cit.*) are a number of alcohols and fatty acids; one notices that these substances are always associated, but the greatest deviations are observed with the substances of lowest molecular weight (as deduced from vapour density); namely, the larger the groups attached to carbinol or carboxyl, the less is the tendency towards association.

Of phenolic compounds but little is known as to the degree of association. Ramsay and Shields's paper (Trans., 1893, **63**, 1101) contains measurements for guaiacol; these furnish association factors of 1·08 between 19·6° and 46·0°, and of 0·96 between 46° and 78°, whilst phenol, on the other hand, exhibits very considerable association (Trans., 1894, **65**, 168). Evidently the methoxyl group is responsible for this hindering of association, whilst the association of phenol itself must be referred to its hydroxyl group, seeing that the parent substance, benzene, is non-associated (*loc. cit.*, p. 1100). But whether the action of the methoxyl group is specific or due also to its position in the molecule cannot immediately be determined from the data given, although the work of Auwers on the molecular weight of phenols in benzene and naphthalene solutions would lead to the conclusion that orientation must have a decided influence.

In conjunction with Bartsch, Beveridge, Dohrn, Ewing, Gierig, Innes, Mann, Orton, Smith, and Walker, Auwers has carried out extensive cryoscopic investigations on the molecular weights of alcoholic and phenolic compounds dissolved in non-hydroxylic solvents (*Zeitsch. physikal. Chem.*, 1893, **12**, 689; 1894, **15**, 33; 1895, **18**, 595;

1896, **21**, 337; 1899, **30**, 300; 1900, **32**, 39; 1903, **42**, 51; *Ber.*, 1895, **28**, 2878; 1898, **31**, 3037). The results obtained have proved conclusively that alcohols and phenols generally form associated molecules in benzene and naphthalene solutions, and also that the association may be inhibited partially or entirely by introduction of substituents ortho to the hydroxyl group in the case of phenolic compounds.

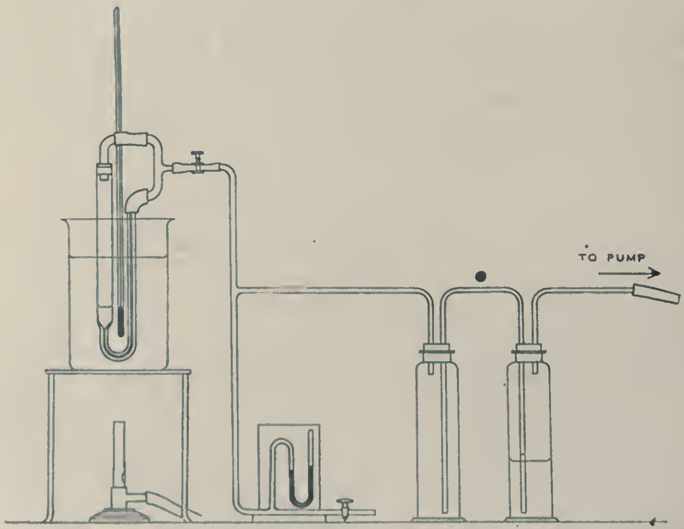
It is consequently a matter of interest to learn whether this non-association is true in the limiting case, namely, when the compound in question is simply fused but not dissolved in another liquid. The results obtained were of such a character as amply to demonstrate the inhibiting influence of ortho-substituents. In calculating the results the original formula given by Ramsay and Shields has been adopted; the results are consequently probably too high in those cases where association occurs, nevertheless the existence of association is indicated and corrections could not very well be applied, as the critical points of the substances examined have only been determined in a few cases, whilst in others they would be indeterminable owing to the decomposition which occurs at higher temperatures.

EXPERIMENTAL.

(a) *Apparatus.*—The apparatus employed in these experiments is of a modified description; on the one hand the errors due to contact with air had to be avoided, on the other the apparatus designed by Ramsay and Shields was inapplicable on account of the fact that several of the substances examined undergo considerable decomposition when raised to their boiling points. A piece of capillary tubing of uniform bore was bent and fused to a larger piece of tubing with a diameter of 2 cm. The wider tube was fitted with a sound rubber stopper through which a tube was inserted, this and the end of the capillary tube being connected with rubber pressure tubing to a T-piece. The third arm of the T-piece was joined by rubber tubing, capable of being closed by a pinch-cock, with a tube connected on the one hand with a gauge, on the other with a Fleuss pump, washing bottles being placed between the pump and the apparatus. The pump was thoroughly overhauled prior to the experiments and was lubricated with an oil of very low vapour-pressure, so that the air-pressure in the whole system could be reduced to a few millimetres. Evacuation was effected when the portion of the apparatus in which the capillary rise was determined was already warm, in this way any air error may be reduced to a negligible amount. The results obtained in the case of phenol itself show a fair agreement with those published by Ramsay, Aston, and Shields, although our numbers for the density deviate somewhat from those given by Kopp. Before an experiment the apparatus was cleaned with alcohol, water, fuming nitric acid, and water, in succession, and was then dried by a current of air at 100°. Before taking a reading of the capillary rise with the cathetometer, the apparatus was tilted so as to ensure complete wetting of the sides of the capillary tube.

The capillary tube was carefully calibrated by measurement of the lengths of several different threads of mercury, and only such tubing was employed as proved to have an even bore.

For a bath, a beaker containing approximately $1\frac{1}{2}$ litres of liquid was employed, the liquids used being water, glycerol, or paraffin; on one occasion concentrated sulphuric acid was employed. With this quantity of liquid and regulation of the heating flame it was possible to keep the temperature within 0·1° for at least fifteen minutes. The temperature was read with two thermometers graduated in tenths of degrees; these had been calibrated by means of the ice point, steam point and the boiling point of bromobenzene.



The densities were measured at some definite temperature by comparison with an equal volume of water and the densities at other temperatures deduced by measurement of the expansion in dilatometers made of glass the coefficient of expansion of which had been determined. Two dilatometers were employed, one with a capacity of about 5 c.c., the other of about 9 c.c., the larger dilatometer being employed in all cases where the amount of material sufficed for the purpose.

Materials Examined.—The source of the materials and guarantee of their purity is briefly stated below.

Phenol.—"Synthetic" phenol of Kahlbaum.

o-*Cresol.*—Obtained from Schuchardt. Refractionated with a rod and disc column (15 discs) and distilled again immediately before use. The substance shows supercooling to a marked extent. For 20° below its melting point the supercooled liquid contracts regularly.

m-*Cresol.*—Merck's "extra pure." The substance gave a benzoyl derivative by the Schotten-Baumann method, which, without any recrystallisation, melted within 1·5° of the correct value. The cresol was fractionated with a rod and disc column and then twice rapidly distilled.

p-*Cresol.*—Obtained from Kahlbaum, fractionated with a rod and disc column, a fraction boiling within 0·25° being collected.

o-*Nitrophenol.*—Prepared from redistilled "absolute" phenol. The product was distilled three times in steam and then dried. On account of the numbers obtained the specimen was once more distilled in a current of steam; recrystallised from methyl alcohol and dried in a vacuum. A repetition of the density and capillarity determinations gave the same value for *K*.

m-*Nitrophenol.*—Purchased from Schuchardt and recrystallised from benzene.

p-*Nitrophenol.*—Prepared at the same time as the ortho-isomeride. The substance was recrystallised from (*a*) concentrated hydrochloric acid, (*b*) water with addition of animal charcoal, (*c*) slightly acidified water.

o-*Chlorophenol.*—Purchased from Schuchardt, once fractionated with rod and disc column, and then rapidly distilled twice. The determinations of density and capillarity were twice effected with practically identical results.

m-*Chlorophenol.*—Purchased from Schuchardt and fractionated (column), boiling point constant.

p-*Chlorophenol.*—Purchased from Schuchardt, fractionated and twice rapidly distilled; the boiling point was within 0·25°.

m-*Bromophenol.*—Prepared by the diazo-reaction from Kahlbaum's pure *m*-bromoaniline; the boiling point of the specimen was constant.

p-*Bromophenol.*—Purchased from Kahlbaum; the melting point was within 1°.

Ethyl Salicylate.—Prepared from salicylic acid, absolute alcohol, and concentrated sulphuric acid. The boiling point was constant within 0·25°. The densities found, being appreciably lower than those given by Delffs (*Jahresb.*, 1854, 26), were re-determined and their values confirmed.

Ethyl m-*Hydroxybenzoate.*—Prepared like the salicylate and recrystallised successively from light petroleum and benzene.

Ethyl p-*Hydroxybenzoate.*—Prepared like its isomerides and recrystallised once from absolute alcohol and twice from benzene.

Benzyl Alcohol.—Made from benzaldehyde by the Cannizzaro reaction, twice fractionated with a rod and disc column, and then twice rapidly distilled.

Benzhydrol.—From benzaldehyde and magnesium phenyl bromide, recrystallised twice from alcohol.

Triphenylcarbinol.—Purchased from Schuchardt; the specimen melted within 1°. As the fused substance slowly darkens, the point of solidification was noted, but no appreciable decomposition had taken place.

Results.

The following record of the results given, the substance, its molecular weight, the temperature (t), the observed capillary rise (h), the radius of the capillary tube (r) and the density (ρ). For economy of space the quantities calculated from these determinations are omitted with the exception of

$$K = \frac{[\gamma(Mv)^{\frac{2}{3}}]_t - [\gamma(Mv)^{\frac{2}{3}}]_t}{t' - t} \quad \text{and} \quad x = \left(\frac{2{\cdot}121}{K}\right)^{\frac{3}{2}}.$$

Substance.	M.W.	t.	h.	r.	ρ.	K.	x.
Phenol	94	53·3°	2·0830	0·03396	1·0434	—	—
		83·0	1·9465	,,	1·0172	1·79	1·30
o-Cresol	108	39·6	2·0827	,,	1·0290	—	—
		67·4	1·9545	,,	1·0040	1·97	1·12
		99·7	1·7985	,,	0·9750	2·04	1·06
m-Cresol	108	19·1	2·1010	,,	1·0324	—	—
		57·6	1·9550	,,	1·0037	1·63	1·48
		99·9	1·7820	,,	0·9683	1·73	1·33
p-Cresol	108	45·5	1·9695	,,	1·0149	—	—
		73·8	1·8690	,,	0·9920	1·54	1·62
		99·8	1·7560	,,	0·9713	1·82	1·26
o-Nitrophenol	139	53·2	1·8635	,,	1·1745	—	—
		79·7	1·7425	,,	1·1486	2·42	0·84
m-Nitrophenol......	139	116·0	2·5193	0·02788	1·3464	—	—
		147·0	2·4130	,,	1·3153	1·62	1·48
p-Nitrophenol	139	129·7	2·1000	0·03396	1·2613	—	—
		162·5	1·9840	,,	1·2329	1·83	1·25
o-Chlorophenol ...	128·5	12·7	1·9415	,,	1·2623	—	—
		45·2	1·8010	,,	1·2293	2·20	1·0
		73·3	1·6550	,,	1·1985	2·00	
m-Chlorophenol ...	128·5	33·0	2·3445	0·02788	1·2573	—	—
		78·6	2·1755	,,	1·2089	1·62	1·49
		138·5	1·8845	,,	1·1522	1·98	1·11
p-Chlorophenol ...	128·5	51·6	1·9060	0·03396	1·2504	—	—
		72·4	1·8255	,,	1·2417	1·86	1·22
		99·8	1·7220	,,	1·2026	2·03	1·08
m-Bromophenol ...	173	44·5	1·5330	,,	1·6221	—	—
		69·5	1·4780	,,	1·5900	1·65	1·45
		100·1	1·3955	,,	1·5543	1·79	1·29

Substance.	M.W.	t.	h.	r.	ρ.	K.	x.
p-Bromophenol ...	173	74·4	1·5390	0·03396	1·5967	—	—
		99·9	1·4640	,,	1·5667	1·88	1·20
Ethyl salicylate ...	166	20·5	1·9420	,,	1·1448	—	—
		61·1	1·8255	,,	1·1141	2·27	0·90
		85·6	1·6870	,,	1·0787	2·30	0·89
Ethyl *m*-hydroxybenzoate.	166	85·8	1·8720	,,	1·1079	—	—
		115·4	1·7675	,,	1·0828	2·14	0·99
		143·5	1·6560	,,	1·0606	2·17	0·97
Ethyl *p*-hydroxybenzoate.	166	119·7	1·7800	,,	1·0984	—	—
		149·3	1·6775	,,	1·0722	2·06	1·04
		172·8	1·5920	,,	1·0495	2·10	1·01
Benzyl alcohol......	108	13·0	2·1960	,,	1·0523	—	—
		47·6	2·0775	,,	1·0250	1·51	1·66
		82·0	1·9470	,,	0·9976	1·64	1·45
Benzhydrol	184	73·55	2·5667	0·02788	1·0636	—	—
		90·9	2·4974	,,	1·0483	2·10	1·01
Triphenylcarbinol..	260	165·8	2·0810	,,	1·0313	—	—
		190·5	2·0001	,,	1·0128	2·11	1·01

Discussion of the Results.

From the measurements recorded in this paper it will be seen that phenolic compounds like the alcohols of the fatty series exhibit association in the liquid condition. It is evident that this association is conditioned by the hydroxyl group, and that such association may undergo steric hindrance by the introduction of groups in the ortho-position. The results obtained for the molecular complexity by the capillarity method closely follow the results of Auwers, using the freezing point method with non-hydroxylic solvents for the detection of the formation of complex molecules.

In the prevention of association two factors have to be taken into account, first the position and secondly the nature of the protecting group. It will be noted in the table of results that in the case of isomerides the effect is most marked (namely, the degree of association is least) when an ortho-compound is examined, and that generally the para-derivatives are more nearly normal than the corresponding meta-isomerides; one naturally arrives at the conclusion that the relative nearness of the positions is represented by the order ortho, para, meta.

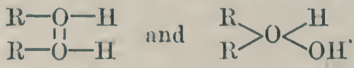
The second factor with regard to the substituent is its intrinsic nature. The maximum effect amongst the group examined is exerted by the nitro- and carbethoxy-groups, followed by the halogens, and finally methyl. One might be inclined to attribute the effect to the negativity of the entrant group were it not that if this is the only quality necessary to prevent association the cresols should show much the same degree of association as phenol itself, whereas experiment proves that *o*-cresol gives very nearly normal values for the constant *K*. We are inclined, in agreement with Victor Meyer and Sudborough, to attribute the effect, at least partly, to the volume of the protecting group, and it was in the hope of confirming our views that we extended the investigation to the phenol carbinols. It might again be argued that the negative nature of the phenyl group was responsible, and an examination of similarly constituted aliphatic alcohols would have been desirable, had not G. Carrara and G. Ferrari (*Gazzetta*, 1906, **36**, 419) already determined the constants for various alcohols which are in favour of the views set forth in this communication. The following table is extracted from their work and gives the association factors for normal primary, secondary, and tertiary butyl alcohols :

Normal alcohol.		Secoudary alcohol.		Tertiary alcohol.	
Temperature.	x.	Temperature.	x.	Temperature.	x.
22—30°	2·978	24—34°	2·191	26—36°	1·934
30—40	2·728	34—41	1·589	36—40	1·515
40—50	1·99	41—52	1·306	40—45	1·268

One peculiar result which attracted attention is the value for x obtained in the case of *o*-nitrophenol. This led to a very careful purification of the compound and a redetermination of its constants ; the result was, however, not affected. We may point out that Carrara and Ferrari (*loc. cit.*) observed similar abnormalities in the case of nitromethame, a substance also of acidic or pseudo-acidic character. The x-values they obtain for this compound vary from 0·935 in the temperature interval 20—31° to 0·809 between 54° and 59°.

The densities of the substances call for little comment, except that the molecular volume of *o*-nitrophenol is markedly greater than that of its isomerides; in fact, the molecular volume of the nitrophenols appears to be greater the less the association.

Evidently since the hydroxyl groups are responsible for the association, a certain amount of "residual affinity" must be ascribed to them, and two possible formulæ immediately suggest themselves, namely :



$$\begin{array}{c} R-O-H \\ \| \\ R-O-H \end{array} \quad \text{and} \quad \begin{matrix} R \\ R \end{matrix}\!>\!O\!<\!\begin{matrix} H \\ OH \end{matrix}.$$

The second of these formulæ would (as Dr. George Young pointed out to one of the authors) correspond to a hydrate of an ether, and must consequently be rejected.

Experiments were instituted to determine the capillarity values of fused azophenols, but had to be abandoned on account of the decomposition these substances undergo above their melting point. Could the research have been further extended in this direction, there is but little doubt that the results of Auwers and Orton would have been confirmed, and the *p*-hydroxyazo-compounds would have exhibited slight association, the *o*-derivatives none. Such behaviour would be in accordance with the formulation of the hydroxyazo-compounds of both series as azophenols rather than as quinone-hydrazones.

East London College.

XLV.—*The Constitution of Hydroxyazo-compounds.*

By WILLIAM BRADSHAW TUCK.

ALTHOUGH the constitution of the ethers, and acetyl and benzoyl derivatives of the hydroxyazo-compounds has been settled definitely by means of their reduction products, chemical methods have failed to decide whether the parent compounds are true hydroxyazo-compounds, $C_6H_5\cdot N\colon N\cdot C_6H_4\cdot OH$, or quinonehydrazones, $C_6H_5\cdot NH\cdot N\colon C_6H_4\colon O$.

In the case of the ethers, for example, it has been found by reduction with tin and hydrochloric acid that benzeneazophenetole,

$$C_6H_5\cdot N\colon N\cdot C_6H_4\cdot OEt,$$

is first converted into benzenehydrazophenetole,

$$C_6H_5\cdot NH\cdot NH\cdot C_6H_4\cdot OEt,$$

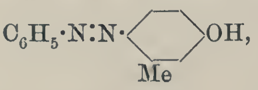
which then undergoes fission into aniline and phenetidine (Jacobsen and Fischer, *Ber.*, 1892, **25**, 995). In this way it is conclusively proved that benzeneazophenetole is a true azo-derivative, that is, its formula is $C_6H_5\cdot N\colon N\cdot C_6H_4\cdot OEt$. Similarly, evidence is available in the case of the acetyl and benzoyl derivatives. It is evident, however, in the case of the free hydroxyazo-compounds that the constitution cannot be determined by reduction, since the two alternative formulæ, $C_6H_5\cdot N\colon N\cdot C_6H_4\cdot OH$ and $C_6H_5\cdot NH\cdot N\colon C_6H_4\colon O$, yield the same first reduction product, $C_6H_5\cdot NH\cdot NH\cdot C_6H_4\cdot OH$. Further, no decisive conclusions can be drawn from substitution compounds owing to the great ease with which additive compounds are produced. From the chemical evidence at our disposal, it is evident that in the case of *p*-hydroxyazo-compounds the ethers and benzoyl derivatives possess the azo-configuration; the same is true for the ethers of the *o*-hydroxyazo-compounds, whilst it is probable that the benzoyl derivatives of the latter are *o*-quinone benzoylphenylhydrazones.

From previous spectrographic work on quinone, hydrazones, and azo-compounds (Baly and Stewart, Trans., 1906, **89**, 502; Baly and Tuck, Trans., 1906, **89**, 982), it seemed probable that conclusive evidence of the structure of the hydroxyazo-compounds could be obtained by an examination of their absorption curves. In the present paper the absorption curves of several of these substances, their ethers and benzoyl derivatives, have been examined, and, as was hoped, it has been possible to decide definitely the constitution of free hydroxyazo-compounds.

The absorption curves were obtained by plotting the oscillation frequencies of the limits of the transmitted light against the logarithms of thicknesses of *M*/10,000 solution equivalent to the concentrations used. The absorption curves are given in Figures 1 to 8, and an examination of these show that the *o*- and *p*-compounds produce a different type of absorption, and for purposes of convenience they will be discussed separately.

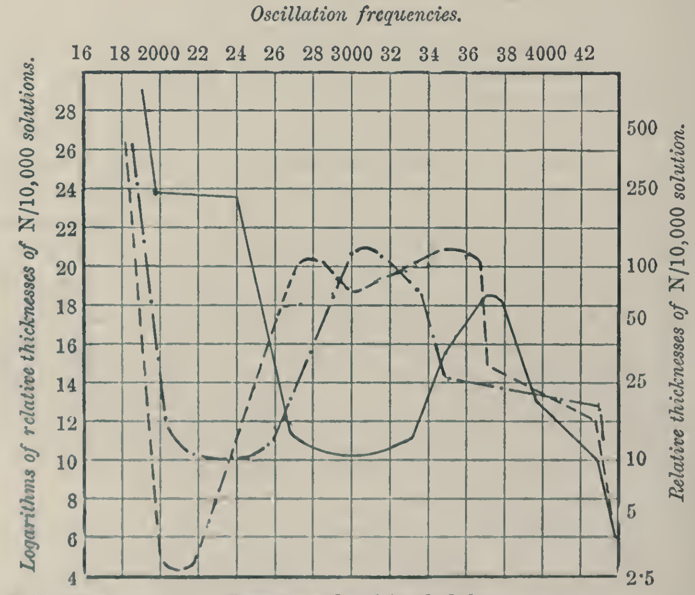
The Para-compounds.

The compounds of this class which have been examined are benzeneazophenol, $C_6H_5 \cdot N \colon N \cdot C_6H_4 \cdot OH$; benzeneazo-*m*-cresol,



and their ethers and benzoyl derivatives. In some cases the effect of hydrochloric acid and sodium ethoxide upon them has been studied.

FIG. 1.



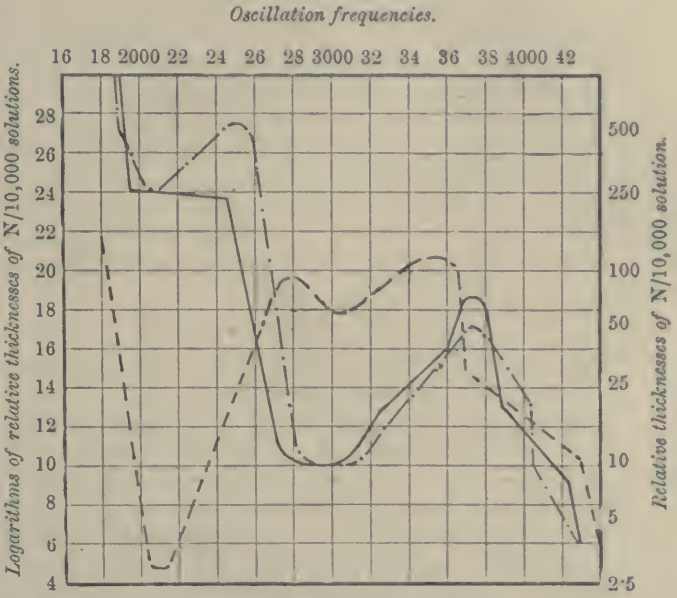
Full curve .... *Benzeneazophenol in alcohol.*
Dotted curve .... ,, *in concentrated hydrochloric acid.*
Dot and dash curve.. ,, *in alcoholic sodium ethoxide.*

In Figs. 1 to 4 the full curves are those of benzeneazophenol, benzeneazophenetole, benzeneazo-*m*-cresol, benzeneazo-*m*-cresetole respectively. The curves for all these substances are very similar, and show a remarkable analogy to that of azobenzene, except that the sudden extension, which occurs between the frequencies 2000 and 2400 in the hydroxyazo-compounds, appears in azobenzene as a well-developed band (Baly and Tuck, Trans., 1906, **89**, 982). The reason for this difference will be discussed later.

The close resemblance of the curves for the ether and hydroxyl compounds proves conclusively that their structure is similar, except that the ethyl group replaces a hydrogen atom. As it is impossible for the ethyl group to be tautomeric, it follows that the hydrogen atom also is not tautomeric under the conditions of the experiment, namely, when the compounds are dissolved in alcohol.

The benzoyl derivative of benzeneazophenol (dot and dash curve, Fig. 2) also shows a very close relation to azobenzene, as was to be expected, since chemical evidence has shown that they have the azo-configuration.

FIG. 2.

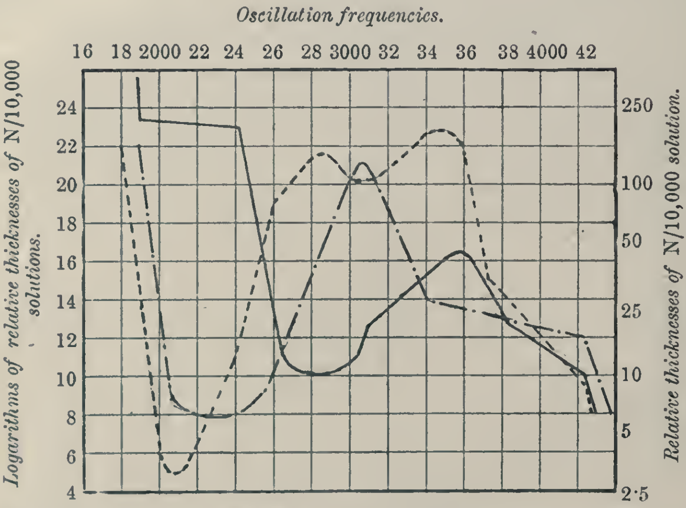


Full curve .... *Benzeneazophenetole in alcohol.*
Dotted curve .... ,, *in concentrated hydrochloric acid.*
Dot and dash curve.. *Benzoylbenzeneazophenol.*

The formula for *p*-hydroxyazo-compounds is therefore of the type $C_6H_5\cdot N:N\cdot C_6H_4\cdot OH$, not $C_6H_5\cdot NH\cdot N:C_6H_4:O$.

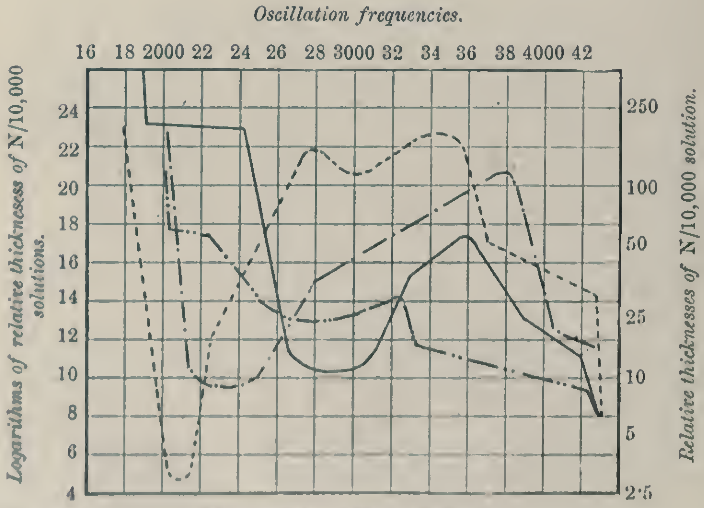
The same conclusion has been recently arrived at (P. Lemoult, *Compt. rend.*, 1906, **143**, 603) by a study of the heats of combustion of these compounds, allowing 27 calories for the thermal characteristic of the azo-group $-N:N-$.

FIG. 3.



Full curve .... *Benzeneazo-*m*-cresol in alcohol.*
Dotted curve .... ,, *in concentrated hydrochloric acid.*
Dot and dash curve.. ,, *in alcoholic sodium ethoxide.*

FIG. 4.



Full curve .... *Benzeneazo-*m*-cresetole in alcohol.*
Dotted curve .... ,, ,, *in concentrated hydrochloric acid.*
Dot and dash curve.. *Azobenzene in concentrated hydrochloric acid.*
Dash and two dots... p-*Benzoquinonebenzoylphenylhydrazone.*

The hydrochlorides of the *p*-hydroxyazo-compounds being very different in colour and reactions from the parent compounds, Hewitt and Pope (*Ber.*, 1897, **30**, 1625) have stated that their constitution must be different, and that they are really hydrochlorides of quinone hydrazones. In view of this, it seems necessary to ascertain the effect that an excess of hydrochloric acid has on the absorption spectra of these substances. An excess of hydrochloric acid is necessary, since the additive compounds hydrolyse with great ease; the ratio of the concentration of the hydrochloric acid to the hydroxyazo-compound was not less than 10,000 : 1. The dotted curves, Figs. 1 to 4, show the effect produced on some of these *p*-hydroxyazo-compounds and their ethers. It may be seen at once that the absorption spectra have altered entirely, and that the change produced is exactly the same in each case. This undoubtedly proves that the hydrochlorides of both the free *p*-hydroxyazo-compounds and of the ethers have similar structures, and consequently the hydrochlorides of the free hydroxyl substances have an azo-structure. It is interesting to compare these with the absorption spectra of azobenzene in a solution containing a large excess of hydrochloric acid (dot and dash curve, Fig. 4).

The Ortho-compounds.

The compounds of this class which have been investigated are benzeneazo-*p*-cresol, *p*-tolueneazo-*p*-cresol, their ethers, and benzoyl derivatives.

The absorption curves (full curves, Figs. 6 and 8) of the ethers agree with those of the ethers of the *p*-compounds, and with that of azobenzene. This was to be expected, as chemical evidence has proved that they are azo-derivatives. The benzoyl derivatives (dot and dash curves, Figs. 6 and 8), on the other hand, give very different spectra. It has been suggested from chemical evidence (Goldschmidt and Brubacher, *Ber.*, 1884, **17**, 352; Oddo and Puxeddu, *Gazzetta*, 1906, **36**, ii, 1) that the benzoyl derivatives of *o*-hydroxyazo-compounds are benzoylphenylhydrazones of *o*-quinone. The absorption curves for the benzoyl derivatives show a very close relation to that of benzoquinonebenzoylphenylhydrazone, synthesised from benzoquinone and benzoylphenylhydrazine, allowing for the fact that the latter is a *p*-quinone and the former an *o*-quinone derivative. There can therefore be no doubt that the benzoyl derivatives are in the quinone-hydrazone form.

The full curves of Figs. 5 and 7, which are those of benzeneazo-*p*-cresol and *p*-tolueneazo-*p*-cresol, show a marked agreement with those of their benzoyl derivatives, so that it may be concluded that the parent compounds are *o*-quinonephenylhydrazones and are derivatives, therefore, of *o*-benzoquinone,

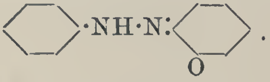


FIG. 5.

Oscillation frequencies.

Upper curves.

Full curve ……	*Benzeneazo*-p-*cresol in alcohol.*
Dotted curve….	,, ,, *in concentrated hydrochloric acid.*
Dot and dash…	,, ,, *in alcoholic sodium ethoxide.*

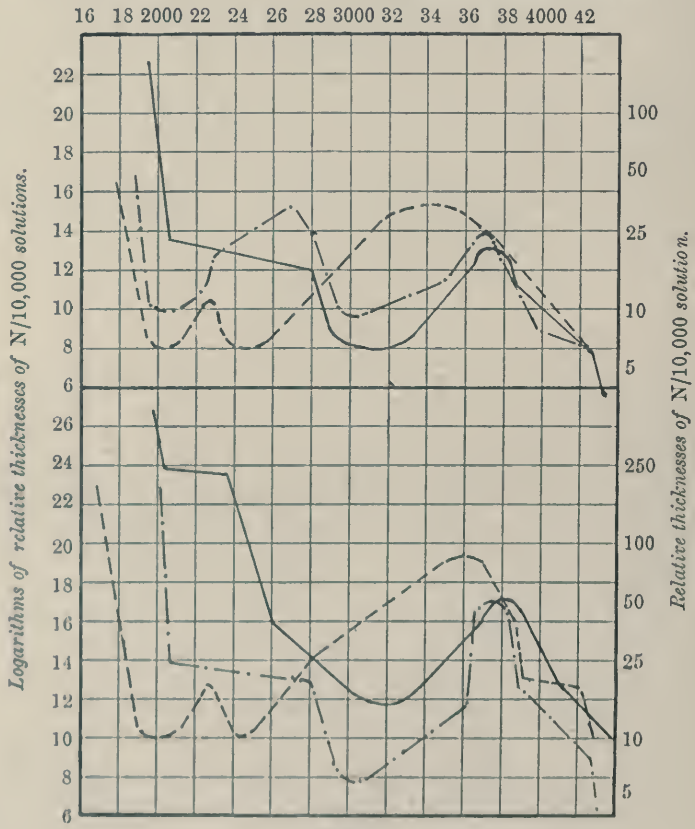


FIG. 6.

Oscillation frequencies.

Lower curves.

Full curve ……	*Benzeneazo*-p-*cresetole in alcohol.*
Dotted curve …	,, ,, *in concentrated hydrochloric acid.*
Dot and dash…	*Benzoylbenzeneazo*-p-*cresol.*

FIG. 7.

Oscillation frequencies.

Upper curves.

Full curve	p-*Tolueneazo*-p-*cresol in alcohol.*
Dotted curve ...	,, ,, *in concentrated hydrochloric acid.*
Dot and dash...	,, ,, *in alcoholic* NaOEt.

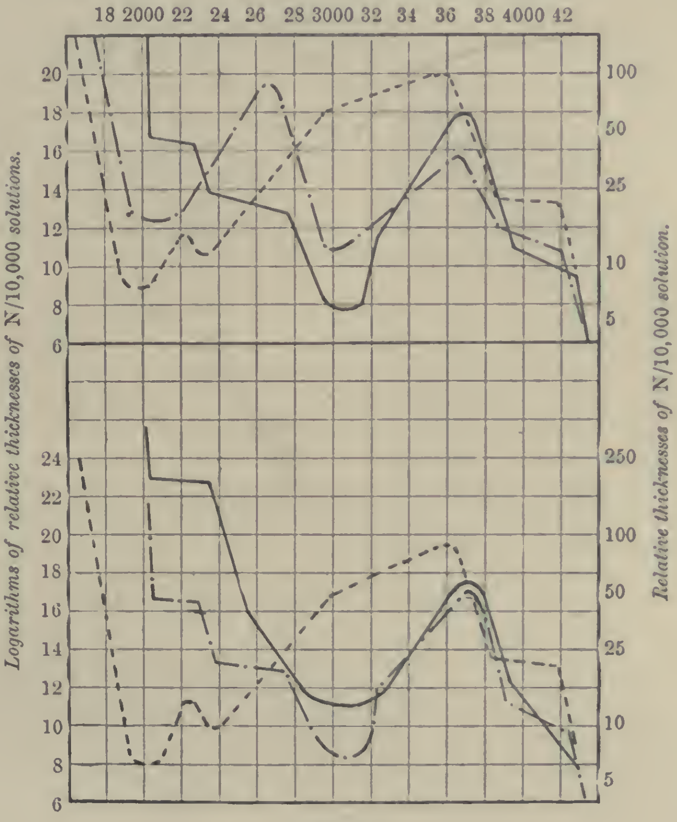


FIG. 8.

Oscillation frequencies.

Lower curves.

Full curve	p-*Tolueneazo*-p-*cresetol in alcohol.*
Dotted curve ...	,, ,, *in concentrated hydrochloric acid.*
Dot and dash...	*Benzoylazo*-p-*cresetole in alcohol.*

The results obtained in this investigation are directly opposed to the hypothesis of "mesohydry" (Oddo and Puxeddu, *loc. cit.*), or equilibrium of the hydrogen between the oxygen and the nitrogen.

Such a state would, from the analogy of enol-keto-tautomerism, undoubtedly produce a characteristic ultra-violet absorption band in the case of the *o*-hydroxyazo-compounds, which would be absent in the benzoyl derivatives. The absence of such a band clearly proves that the hydrogen is not in the tautomeric condition required by the hypothesis of mesohydry.

In the *o*-compounds the effect of hydrochloric acid on both the ethers and the parent compounds is exactly the same (dotted curves, Figs. 5 to 8). From this it may be concluded that both hydrochlorides have the same structure, and that as the ethers are in the azo-form, the hydrochlorides of the parent compounds must also be in that form. Thus the effect of adding hydrochloric acid to *o*-hydroxyazo-compounds is to change them from *o*-quinonehydrazones to azo-derivatives:

$$C_6H_5\cdot NH\cdot \underset{(1)}{N}\colon C_6H_4\colon O + HCl \longrightarrow C_6H_5\cdot N\colon N\cdot C_6H_4\cdot OH + HCl.$$

The reason for this change probably lies in the fact that the hydrochloric acid in adding on to the nitrogen atom (1) causes the latter to become more nearly saturated and therefore less able to retain the hydrogen atom against the great attraction of the oxygen.

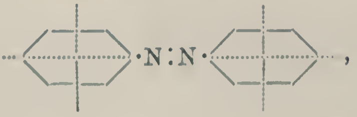
The relation of the absorption curves of the various azo-compounds to one another is of great interest. From the curves given it may be seen that when a large amount of residual affinity is in close proximity to one of the benzene nuclei of azobenzene as in the case of the hydroxyl compounds and their ethers,

$$C_6H_5\cdot N\colon N\cdot C_6H_4\cdot OH \text{ and } C_6H_5\cdot N\colon N\cdot C_6H_4\cdot OEt,$$

a very great diminution in the persistence of the colour band occurs. If the residual affinity of the hydroxyl group is decreased by replacing the hydrogen atom by an acetyl or benzoyl group, the curves obtained approach more nearly to that of azobenzene.

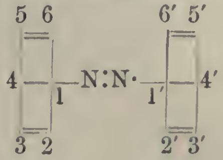
It has been shown (Baly and Collie, Trans., 1905, **87**, 1332) that unsaturation in the α-position to a benzene ring produces a very great alteration in the type of vibration.

These facts are of considerable interest in view of the hypothesis, recently put forward, with regard to the colour of azobenzene (Baly and Tuck, Trans., 1906, **89**, 982). According to this view the colour depends on the fact that the benzene nuclei vibrate mainly along the two directions indicated by the dotted lines,

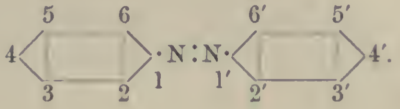


,

the extreme phases being



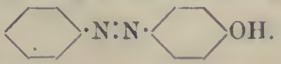
and



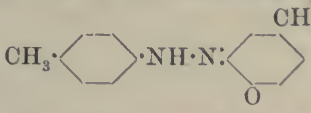
Thus the carbon atoms 1 and 1′ are to a large extent unsaturated and the action of these centres of unsaturation on the unsaturated group ·N:N· sets up the isorropesis. From this it may be seen at once that the more the vibrations of the benzene rings are disturbed the greater will be the diminution of the persistence of the isorropesis band observed. This agrees with the results previously obtained by substitution in benzoquinone (Stewart and Baly, Trans., 1906, **89**, 618). Addition of sodium ethoxide to solutions of the ethers of hydroxyazo-compounds produces absolutely no change, but when added to the free hydroxyl compounds, a considerable modification of the type of absorption occurs.

Conclusions.

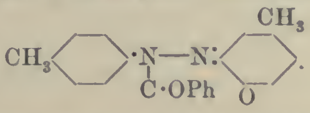
1. The *p*-hydroxyazo-compounds and their hydrochlorides are in the true azo-form, for example, benzeneazophenol is



2. The *o*-hydroxyazo-compounds and their benzoyl derivatives are derivatives of *o*-benzoquinonebenzoylphenylhydrazone, for example, the formulæ of *p*-tolueneazo-*p*-cresol and its benzoyl derivatives are



and



3. The hydrochlorides of the *o*-hydroxyazo-compounds are derivatives of true azo-compounds.

I should like to express my hearty thanks to Prof. Collie and Mr. Baly for the interest they have taken in the progress of these experiments. I also wish to thank Mr. Baly for the facilities he has afforded me in carrying out this research. I am indebted to the Chemical Society for a grant in aid of the work.

The Spectroscopic Laboratory,
University College,
London.

XLVI.—*Resolution of Tetrahydro*-p-*toluquinaldine into its Optically Active Components.*

By William Jackson Pope and Thomas Constantine Beck.

The methods of resolving externally compensated bases into their optically active components, which have been developed by Pope, Peachey, Rich, and Harvey (Trans., 1898, **73**, 893; 1899, **75**, 1066, 1093, and 1127), have led to the accumulation of evidence proving that optical activity results from asymmetry, not only of the carbon atom, but also of nitrogen, sulphur, selenium, and tin atoms in the quinque- and quadri-valent states of combination. The application of these methods involves the use of a strong optically active acid, and those available for the described purpose have hitherto been the *d*- and *l*-$a\pi$-bromo- and chloro-camphorsulphonic acids of Kipping and Pope (Trans., 1895, **67**, 354) and the *d*- and *l*-β-camphorsulphonic acids of Reychler (Trans., 1899, **75**, 1105); the use of the *d*- and *l*-π-camphorsulphonic acids of Kipping and Pope (Trans., 1893, **63**, 548) for this purpose is necessarily limited by the difficulty of preparing these acids in large quantities.

As the usefulness of the methods in question would obviously be extended if strong optically active acids other than those above-mentioned were available, it seemed desirable to examine the applicability of the *d*-$a\beta$-bromocamphorsulphonic acid of Armstrong and Lowry (Trans., 1902, **81**, 1441) in connexion with the Pope and Peachey method. The most specialised case of the method is that of Pope and Rich (Trans., 1899, **75**, 1093), in which crystallisation is induced in a solution containing two equivalents (*d*-*B*, *l*-*B*, 2HCl) of the hydrochloride or other salt of an externally compensated base, and one equivalent of an alkali or ammonium salt (NH_3, *d*- or *l*-*A*) of an optically active acid; the reaction proceeds in accordance with the following equation:

$$d\text{-}B,\ HCl + l\text{-}B,\ HCl + NH_3,\ d\text{-}A = d\text{-}B,\ d\text{-}A + l\text{-}B,\ HCl + NH_3,HCl.$$

As has been previously shown, the least soluble salt (*d*-*B*, *d*-*A*, or *l*-*B*, *d*-*A*), of which the formation is possible in the system, crystallises out, leaving ammonium and the other component of the externally compensated base in solution as the more soluble salt with a mineral acid (*l*-*B*, HCl).

In view of the rapidity and convenience of this method of working, we have again investigated the resolution of externally compensated tetrahydro-*p*-toluquinaldine into its optically active components in order to ascertain whether the *d*-$a\beta$-bromocamphorsulphonic acid of

Armstrong and Lowry can be usefully employed in carrying out the method of resolution.

*Resolution of Tetrahydro-*p*-toluquinaldine.*

On adding to a concentrated warm aqueous solution of externally compensated tetrahydro-*p*-toluquinaldine hydrochloride (two equivalents) an aqueous solution of ammonium *d*-*αβ*-bromocamphorsulphonate (one equivalent), and allowing to cool, a nearly quantitative separation of crystalline *d*-tetrahydro-*p*-toluquinaldine *d*-*αβ*-bromocamphorsulphonate occurs. After recrystallisation from ethyl acetate the salt is obtained in colourless needles melting at 170—172°; it is readily soluble in alcohol or moist acetone, and sparingly so in ethyl acetate or water:

0·1763 gave 0·3435 CO_2 and 0·1003 H_2O. C = 53·13; H = 6·32.
0·2297 ,, 0·4502 CO_2 ,, 0·1305 H_2O. C = 53·45; H = 6·31.
$C_{21}H_{30}O_3NBrS$ requires C = 53·39; H = 6·21 per cent.

0·3142 gram, made up to 25 c.c. with water, gave α_D +2·37° in a 200 mm. tube; whence $[\alpha]_D$ +94·3° and $[M]_D$ +445°.

On treating the salt with soda it yielded *d*-tetrahydro-*p*-toluquinaldine which had the specific rotatory power of $[\alpha]_D$ +79·3° in a 2 per cent. benzene solution, and otherwise corresponded with the base obtained by Pope and Rich (*loc. cit.*).

The crude *l*-base liberated on adding caustic soda to the mother liquors remaining after the first separation of the salt of the *d*-base, after solution in hydrochloric acid, is conveniently treated with ammonium *d*-*απ*-bromocamphorsulphonate, as described by Pope and Rich, for the purpose of separating from it pure *l*-tetrahydro-*p*-toluquinaldine *d*-*απ*-bromocamphorsulphate. In an actual experiment it was found that 26 grams of externally compensated base yielded by one treatment as described with each of the isomeric bromocamphorsulphonic acids 10·5 grams of pure *d*-base and 7·5 grams of the pure lævo-isomeride.

l-*Tetrahydro*-p-*toluquinaldine* d-*αβ-Bromocamphorsulphonate.*

For purposes of comparison it was convenient to prepare *l*-tetrahydro-*p*-toluquinaldine *d*-*αβ*-bromocamphorsulphonate from pure *l*-base and *d*-acid; the salt crystallised in colourless, flattened needles melting at 171—172°:

0·2850 gave 0·5561 CO_2 and 0·1650 H_2O. C = 53·21; H = 6·43.
0·2831 ,, 0·5544 CO_2 ,, 0·1633 H_2O. C = 53·41; H = 6·40.
$C_{21}H_{30}O_3NBrS$ requires C = 53·39; H = 6·21 per cent.

0·2659 gram, made up to 25 c.c. with water, gave $\alpha_D + 0·74°$ in a 200 mm. tube; whence $[\alpha]_D$ $+34·8°$ and $[M]_D + 164·2°$.

The two salts, *d-B*, *d-A*, and *l-B*, *d-A*, thus have the molecular rotatory powers $+164·2°$ and $+445°$ respectively; the sum of these values is twice the molecular rotatory power of the acid ion and the difference is twice the molecular rotatory power of the basic ion. The molecular rotatory power calculated for the ion of the *d*-acid is thus $+304·5°$ and that for the ion of the *d*-base is $+140·4°$. The latter value agrees closely with the value $+139·5°$ obtained by Pope and Rich for the hydrochloride; the former value is practically identical with that of $+304·3°$ deduced below from the examination of the ammonium and calcium salts of *d*-$\alpha\beta$-bromocamphorsulphonic acid.

0·4348 gram of calcium *d*-$\alpha\beta$-bromocamphorsulphonate dried at 100°, made up to 25 c.c. with water, gave α_D $+3·21°$ in a 200 mm. tube; whence $[\alpha]_D$ $+92·3°$ and $[M]_D$ $+304·5°$.

0·9004 gram of ammonium *d*-$\alpha\beta$-bromocamphorsulphonate, containing $2H_2O$, made up to 25 c.c. with water, gave $\alpha_D + 7·55°$ in a 200 mm. tube; whence $[\alpha]_D$ $+83·55°$ and $[M]_D$ $+304·1°$.

It is thus shown that another strong optically active acid, in addition to those previously used, is available for the resolution of externally compensated bases into their optically active components. We are at present engaged in studying the resolution of externally compensated bases containing asymmetric atoms other than those of carbon with the aid of this acid.

MUNICIPAL SCHOOL OF TECHNOLOGY,
VICTORIA UNIVERSITY OF MANCHESTER.

XLVII.—*Displacement of Halogens by Hydroxyl. I. The Hydrolytic Decomposition of Hydrogen and Sodium Monochloroacetates by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities.*

By GEORGE SENTER.

IN the course of certain experiments on the temperature-coefficients of chemical reactions, I had occasion to investigate the mechanism of the displacement of chlorine by hydroxyl in chloroacetic acid and some of its salts. As the preliminary observations indicated that the reactions were not so simple as had been anticipated, and the results promised to be of interest for the general question of chemical dynamics, the problem was studied systematically, and the present paper contains an account of the results so far obtained.

The hydrolytic decomposition of chloroacetic acid by hot water was investigated by Buchanan (*Ber.*, 1871, **4**, 863), and later in van't Hoff's laboratory by Schwab (van't Hoff, *Studien zur Chemischen Dynamik*). It proceeds quantitatively according to the equation $CH_2Cl \cdot CO_2H + H_2O = OH \cdot CH_2 \cdot CO_2H + HCl$, and is therefore a unimolecular reaction, as Schwab found. The rate of decomposition of sodium chloroacetate by sodium hydroxide was also investigated by Schwab (*loc. cit.*); in dilute solution it is represented by the equation $CH_2Cl \cdot CO_2Na + NaOH = OH \cdot CH_2 \cdot CO_2H + NaCl$, and is of interest as being the chemical change on which van't Hoff based his treatment of bimolecular reactions. Further, the rate of decomposition of certain chloroacetates by water at high temperatures has been investigated by Kastle and Keiser (*Amer. Chem. J.*, 1893, **15**, 471), who found that the reaction velocity is almost independent of the base with which the chloroacetic acid is combined. Within the last few months, Euler (*Ber.*, 1906, **39**, 2726) has published the results of some experiments on the rate of reaction between silver nitrate and chloroacetic acid and certain other halogen compounds. The general question of the reactivity of organic halogen compounds has been dealt with by many investigators, more particularly by Hecht, Conrad, and Bruckner (*Zeitsch. physikal. Chem.*, 1889—1891, **3**—**7**), by Nef (*Annalen*, 1899, **309**, 126), and by Burke and Donnan (Trans., 1904, **85**, 555), but in no case has the mechanism of the change been satisfactorily elucidated.

In the present paper it is shown, by varying the initial concentration, that the hydrolysis of chloroacetic acid, according to the equation $CH_2Cl \cdot CO_2H + H_2O = OH \cdot CH_2 \cdot CO_2H + HCl$ is strictly proportional to the acid concentration within wide limits; the reaction velocity is not greatly affected by hydrogen chloride, or by such neutral salts as sodium chloride and potassium nitrate in normal solution.

The rate of decomposition of sodium chloroacetate in aqueous solution at 102° has also been measured; in dilute solution it is unimolecular, but stronger solutions show slight deviations from the simple law. The rate of reaction is diminished by certain neutral salts.

The rate of interaction of sodium chloroacetate and sodium and potassium hydroxides at 102°, according to the equation

$$CH_2Cl \cdot CO_2Na + NaOH = OH \cdot CH_2 \cdot CO_2Na + NaCl,$$

has also been measured; only in dilute solution is the action strictly bimolecular. The rate of change was accelerated by all the neutral salts tried without exception.

It is further shown that sodium chloroacetate is hydrolysed by water at about 1/10th of the rate at which $N/10$ sodium hydroxide effects the change, and that the former reaction is scarcely affected by hydrogen chloride, results which are not in accord with current views as to the relative activity of water and alkali as hydrolytic agents. The influence of neutral salts on the rate of chemical reactions in which OH' ions take part is considered in the light of the results given in this paper and of those previously obtained by Arrhenius (*Zeitsch. physikal. Chem.*, 1887, 1, 110). As bearing on these observations, the general question of the effect of neutral salts in accelerating certain chemical reactions, more particularly those in which dilute acids are concerned (for which much experimental material is available), is discussed in the following section.

Effect of Neutral Salts on the Activity of Acids.

It has long been known that the activity of dilute acids, as shown, for example, in the catalytic effect they exert on the hydrolytic decomposition of sucrose, is increased by the addition of neutral salts which themselves do not effect the hydrolysis; this effect may shortly be designated "neutral salt action." On account of its importance for the theory of solutions, this phenomenon has been often investigated, more particularly by Löwenthal and Lenssen (*J. pr. Chem.*, 1862, **85**, 321, 401), Spohr (*J. pr. Chem.*, 1886, **33**, 272), Arrhenius (*Zeitsch. physikal. Chem.*, 1889, **4**, 226; 1899, **31**, 197), and Kay (*Proc. Roy. Soc. Edin.*, 1898, **22**, 484). The general outcome of the investigations has been to show that in all cases the reaction is accelerated by compounds which are highly ionised in aqueous solution, whilst non-electrolytes have practically no effect. The essential features of the phenomenon are shown in the accompanying table, which gives the results obtained by Arrhenius for the rate of inversion of a 10 per cent. solution of sucrose; the concentration of acid and salt, the temperature, and the velocity constant are given in the table:

Magnitude of Neutral Salt Action (Arrhenius).

Composition of solution.	Temperature.	k.	Increase per cent.
0·05 HCl	39·5°	31·9	—
+ 0·4 $NaCl$	,,	36·8	25·3
+ 0·4 $LiCl$	,,	36·9	26·4
+ 0·4 NH_4Cl	,,	37·0	26·4
+ 0·2 $CaCl_2$	,,	37·5	26·9
+ 0·2 $MgCl_2$	,,	37·4	26·5
0·0005 HCl	53·8	17·7	—
+ 0·18 $HgCl_2$	,,	18·0	1·7

The most striking fact shown by the table is that in equivalent solution neutral salts which are electrolytes exert practically the same effect. As the neutral salt action is proportionately greater the more dilute the acid solution, it follows that the chlorides referred to in the first part of the table are at least twenty times more active than mercuric chloride.

Several suggestions have been made to account for neutral salt action. Löwenthal and Lenssen were of opinion that it was due to the salts combining with water, the concentrations of the reacting substances being thus increased. Arrhenius at first considered that it was due to the effect of the ions of the salt on the hydrogen ions; in his latest pronouncement on the subject he suggests that the neutral salts increase the osmotic pressure of the sucrose (*Text-Book of Electrochemistry*, p. 109). In a recent paper, R. J. Caldwell (*Proc. Roy. Soc.*, 1906, **78**, *A*, 272), working under the direction of Prof. Armstrong, has revived the suggestion of Löwenthal and Lenssen; he considers that, in consequence of the withdrawal of part of the water to form a hydrate with the neutral salt, the ratio of acid to "free" solvent is increased; in other words, the acid solution becomes more highly concentrated, and the hydrolysis of the sugar is effected more rapidly. From the amount of water which must be added to reduce the velocity constant to the normal value, the amount of water in combination with the salt—the degree of hydration—is obtained. The values at 25° are as follows: $KCl,10H_2O$; $NaCl,13H_2O$; $BaCl_2,19H_2O$; $CaCl_2,22H_2O$.

With the view of testing the above hypothesis, Caldwell has compared the degrees of hydration thus arrived at with those obtained by Jones and his co-workers (*Zeitsch. physikal. Chem.*, 1906, **55**, 355) by other methods; the agreement is satisfactory only for two of the instances quoted above. This, however, is perhaps not to be regarded as an argument against the hypothesis, as the degrees of hydration calculated by Jones do not appear very trustworthy; in particular, the rapid increase of hydration with dilution which he obtains in some cases is in opposition to the requirements of the law of mass action. It seems desirable, therefore, to test the consequences of the hydrate hypothesis of neutral salt action more fully. In the following paragraphs, on the basis of the summary of experimental results given above (1) the relative neutral salt action of different salts, (2) the effect of temperature, (3) the effect of neutral salts on other reactions, are considered, and the conclusion is drawn that the hydrate hypothesis does not account for the experimental facts.

(1) *The Comparative Effects of Different Salts.*—There is a good deal of evidence, which cannot be given here in detail (compare Baur, *Ahrens' Sammlung*, 1903, **8**, 478; Geffcken, *Zeitsch. physikal. Chem.*, 1904, **49**, 257), to the effect that nitrates of alkali metals are only

slightly, if at all, hydrated in solution, and that the degree of hydration increases from chlorides to sulphates; this behaviour is exactly what is to be expected from the known properties of the solid salts. There is no such variation of neutral salt action; the results of Arrhenius, Spohr, Kay, and others show that in equivalent solution the effect is practically independent of the nature of the salt, the activity of potassium chloride and nitrate being the same as that of calcium and magnesium chloride in equivalent solution (compare table, p. 462). As regards positive groups, Kohlrausch (*Proc. Roy. Soc.*, 1903, **71**, 338), from measurements of the relative migration velocity of sodium, potassium, and lithium ions, has expressed the opinion that the latter are most highly hydrated in solution, and the same conclusion has been reached in another way by Jones (*Zeitsch. physikal. Chem.*, 1906, **55**, 429). Consequently, if the hydrate hypothesis of neutral salt action is tenable, lithium salts ought to have a much greater effect than sodium and potassium salts with the same negative ion, but the observations of Arrhenius and of Kay (*loc. cit.*) show conclusively that this is not the case.

(2) *The Effect of Change of Temperature on Neutral Salt Action.*—Various considerations lead to the conclusion that if hydrates exist in solution, their complexity must decrease rapidly with rise of temperature. Thus it is a well-known fact that the higher the temperature, the smaller is the number of molecules of solvent with which salts separate from solution. Further, the amount of heat evolved when salts combine with water is generally large, and from the Horstmann-van't Hoff law on the relation between heat development and displacement of equilibrium it follows at once that the number of water molecules associated with the solute must diminish rapidly with rise of temperature. In accordance with these *a priori* considerations, Jones (*loc. cit.*, p. 430) considers that "the greater part of the water can be withdrawn from these compounds at temperatures only a little above 100°.

In striking contrast to these observations, the effect of change of temperature on neutral salt action is very slight. Arrhenius found that the increase in the activity of hydrobromic acid due to the addition of 0·4 mol. potassium bromide at 25°, 39·4°, and 52° amounted to 32, 36, and 33 per cent. respectively. Spohr (*loc. cit.*) and Euler (*Zeitsch. physikal. Chem.*, 1900, **32**, 348) found a very slight decrease of the neutral salt effect with rise of temperature. These observations cannot readily be reconciled with the suggestion that the effect in question is due to hydrate formation.

(3) *The Effect of Neutral Salts on other Reactions.*—This may be illustrated by the action of sodium chloride on the rate of a simple unimolecular reaction, for example, the hydrolytic decomposition of

carbon oxysulphide, COS, by water at 25°, investigated by Bückbock (*Zeitsch. physikal. Chem.*, 1900, **34**, 229). If sodium chloride takes up a large proportion of water, the ratio between the oxysulphide and the free solvent will be increased, and a greater rate of hydrolysis may be expected. As a matter of fact, the rate is practically the same in *N*-sodium chloride solution and in pure water.

These conclusions are confirmed by the results with neutral salts described in the present paper, and some evidence is adduced to show that the earlier suggestion of Arrhenius, that neutral salt action is due to the action of the ions of the salt on $H^{\cdot}$ or OH' ions, has most in its favour. It is quite possible that in some cases neutral salts may accelerate chemical actions owing to association with the solvent, but the general phenomenon does not seem to be adequately accounted for in this way.

EXPERIMENTAL.

Methods of Measuring Velocities.

The chloroacetic acid used in the investigation was obtained from Kahlbaum; its purity was controlled by titration with standard alkali. The neutral salts were also Kahlbaum's preparations. The sodium chloroacetate solutions were prepared by mixing solutions of chloroacetic acid and sodium hydroxide of equivalent strength. Distilled water, free from carbon dioxide, was used in preparing the solutions and in the titrations.

A constant temperature for the experiments was attained by means of a thermostat filled with glycerol and provided with an Ostwald thermoregulator containing quinoline. As the majority of the experiments were made at high temperatures, water could not be used as the thermostat liquid, but glycerol proved satisfactory in every way. The temperature remained constant throughout an experiment to 0·2°, in most cases to 0·1°, but as in all cases comparison experiments were made, the results described in the present paper are practically independent of slight changes of temperature.

The reacting substances, enclosed in sealed Jena glass tubes which had previously been carefully steamed out, were heated at the required temperature for definite periods, then cooled rapidly to the ordinary temperature (which practically stopped the reaction) and titrated. In the experiments with chloroacetic acid and with sodium chloroacetate, the course of the reaction was followed by titrating the acid with *N*/10 ammonia, using lacmoid as indicator. It was shown by preliminary experiments that this method gives trustworthy results, not only with the mixture of hydrochloric and glycollic acids resulting from the hydrolysis of chloroacetic acid, but also in the presence of such neutral salts as sodium chloride and potassium nitrate. In the experiments with sodium hydroxide, the free alkali was titrated with *N*/20 sulphuric acid, using lacmoid as indicator; this method is also trustworthy in the presence of the neutral salts employed in the present series of experiments.

Although, from considerations of space, only one set of experiments is usually quoted, the results were confirmed by two or three independent series of observations, the agreement being in all cases satisfactory.

Results.

Hydrolysis of Chloroacetic Acid.—As the constants for a unimolecular reaction, calculated from Schwab's results, are somewhat irregular, it was considered desirable to determine the order of the reaction more conclusively by varying the initial concentration within fairly wide limits. The experiments were carried out at 102°, as described above. The values of $k = 1/t \log C_o/C_t$ where t represents the time in minutes, and C_o and C_t the initial concentration and that at the time t respectively, are given in Table I:

TABLE I.—Temperature 102°.

Chloroacetic acid concentration.	$k = 1/t \log C_o/C_t$.	Chloroacetic acid. concentration.	$k = 1/t \log C_o/C_t$.
N/2…………	0·00046	*N*/8…………	0·00048
N/4…………	0·00048	*N*/16 ………	0·00049

It is clear from these results that, within the limits of experimental error, the rate of reaction is strictly proportional to the chloroacetic acid concentration.

As the constants do not decrease to any appreciable extent during the reaction, it follows that the hydrochloric acid produced in the course of the decomposition has very little effect. To test this point further, a series of experiments was carried out with *N*/4 chloroacetic acid and varying concentrations of hydrochloric acid, the results of which are given in Table II. The chloroacetic acid concentration, C_t, is expressed in c.c. of *N*/10 ammonium hydroxide required for neutralisation:

TABLE II.

Chloroacetic acid *N*/4. Temperature 102°.

	No HCl.		*N*/4 HCl.		*N*/2 HCl.	
t (min.).	C_t.	k.	C_t.	k.	C_t.	k.
0	24·9	—	24·9	—	24·9	—
900	16·1	0·00048	16·9	0·00043	17·3	0·00040
3240	6·0	0·00044	6·4	0·00042	6·9	0·00040

From these results it is clear that hydrochloric acid exerts a slight retarding effect; if we compare the first stage of the reaction when no acid is added with that in the presence of *N*/2 acid, it appears that the latter retards the change in the ratio 48 : 40.

The influence of sodium chloride and potassium nitrate on the reaction has been studied at 102° with the following results:

Composition of solution.	*k*.
N/5-Chloroacetic acid	0·00051
,, ,, + *m*/1 NaCl	0·00051
,, ,, + *m*/1 KNO_3	0·00053

The probable mechanism of the reaction will now be considered. Chloroacetic acid is a comparatively weak acid; from the value of the dissociation constant, as given by Ostwald, it can readily be shown that in *N*/4 solution it is approximately *N*/50 with regard to $H^{\cdot}$ and $CH_2Cl{\cdot}CO_2'$ ions. According to the law of mass action, the

$$CH_2Cl{\cdot}CO_2'$$

ion concentration is reduced to a small fraction (less than 1/10) of its original value by the addition of *N*/2 HCl, which does not seriously affect the reaction velocity; it thus appears that it is the undissociated acid which undergoes hydrolytic decomposition. Similar reasoning shows that OH′ ions are not concerned in the time reaction, which may therefore be represented by the equation

$$CH_2Cl{\cdot}CO_2H + H_2O = OH{\cdot}CH_2{\cdot}CO_2H + HCl.$$

An explanation on the lines of that suggested by Lobry de Bruyn and Steger for the reaction between ethyl iodide and sodium ethoxide, that the time reaction is the dissociation of the halogen alkyl with liberation of halogen ions, cannot apply in this case, because sodium chloride does not affect the reaction velocity.

Bevan (*Proc. Camb. Phil. Soc.*, 1906, 13, 269), who has followed this reaction by means of conductivity measurements, has obtained evidence of a period of induction, and a possible explanation of this observation is that the water and chloroacetic acid unite to form a compound which breaks down into glycollic and hydrochloric acids. It may be suggested that the compound in question is $CO_2H{\cdot}CH_2Cl{<}\begin{smallmatrix}OH\\H\end{smallmatrix}$, the chlorine becoming tervalent, and that the reaction completes itself by elimination of hydrochloric acid. It remains to decide whether it is the rate of formation or the rate of decomposition of this compound which is actually measured. The observation that hydrochloric acid retards the rate of reaction, as shown above, appears to indicate that the latter alternative is the correct one.

Hydrolytic Decomposition of Sodium Chloroacetate by Water.—The chloroacetate solutions were prepared by mixing equivalent solutions of the acid and sodium hydroxide and diluting to the required strength. The experiments were carried out as described above. The following typical results indicate the course of the reaction in dilute solution, the concentrations being expressed in c.c. of $N/10$ ammonium hydroxide equivalent to the (combined) acid present.

TABLE III.—Temperature 102°.

Sodium chloroacetate, 0·2 molar (10 c.c.).

t (min.).	C_{salt}.	k.
0	20·0	—
120	16·0	0·00185
240	12·7	0·00188
360	10·4	0·00182
1560	3·6	0·00108

Sodium chloroacetate, 0·05 molar (20 c.c.).

t (min.).	C_{salt}.	k.
0	10·0	—
120	8·2	0·00165
240	6·7	0·00167
360	5·6	0·00161
1560	2·0	0·00104

Sodium chloroacetate, 0·2 molar.

t (min.).	C_{salt}.	k.
0	19·9	—
60	17·7	0·00195
180	14·1	0·00189
300	11·3	0·00189

Sodium chloroacetate, 1·0 molar.

t (min.).	C_{salt}.	k.
0	99·5	—
60	77·0	0·00425
180	48·8	0·00395
300	35·3	0·00345

It will be observed that in the more dilute solutions the rate of reaction is strictly proportional to the chloroacetate concentration until half the reaction is complete, beyond which point it diminishes greatly. In stronger solutions the constants diminish somewhat during the first stage of the reaction.

It will further be observed that the value of k for a unimolecular reaction is much greater for a molar than for a 1/10 molar solution. In order to determine how the value of k varies with the amount of salt present, a series of observations was made with widely different initial concentrations; the results of which are given in Table IV:

TABLE IV.—Temperature 102°.

Sodium chloroacetate concentration.	k.	Sodium chloroacetate concentration.	k.
1·0 molar	0·00395	0·1 molar	0·00170
0·5 ,,	0·00240	0·05 ,,	0·00166
0·2 ,,	0·00189	0·025 ,,	0·00165

For solutions less than 0·1 molar, the velocity is practically independent of the concentration, as required for a unimolecular reaction; with stronger solutions it increases rapidly with increasing concentration.

A few experiments were made to determine whether the rate at which chlorine is replaced by hydroxyl varies according to the base with which the chloroacetic acid is combined. The results of typical experiments are given in the accompanying table:

TABLE V.—Temperature 102°.

	$CH_2Cl{\cdot}CO_2Na$ m/5.		$CH_2Cl{\cdot}CO_2K$ m/5.		$(CH_2Cl{\cdot}CO_2)_2Ba$ m/10.	
t (min.).	C_{salt}.	k.	C_{salt}.	k.	C_{salt}.	k.
0	19·9	—	19·9	—	19·9	—
60	17·7	0·00195	17·5	0·00201	17·9	0·00185
180	14·2	0·00187	14·2	0·00187	14·4	0·00180
330	10·8	0·00184	10·6	0·00191	11·0	0·00180

These numbers show that, within the limits of experimental error, the salts undergo hydrolysis at the same rate, independently of the nature of the base, as Kastle (*loc. cit.*) also found.

Influence of Neutral Salts.—The influence of solutions of sodium and potassium chlorides and nitrates on the rate of reaction has been measured and the results are summarised in the accompanying table:

TABLE VI.—Temperature 102°.

Composition of solution.	$k=1/t\log C_0/C_t$.
Sodium chloroacetate m/10	0·00172
,, ,, ,, + NaCl m/2	0·00135
,, ,, ,, + NaCl m/1	0·00103
,, ,, ,, + $NaNO_3$ m/1	0·00172
Sodium chloroacetate m/5	0·00180
,, ,, ,, + NaCl m/1	0·00130
,, ,, ,, + KCl m/1	0·00160
,, ,, ,, + KNO_3 m/1	0·00178
Potassium chloroacetate m/5......................	0·00185
,, ,, ,, + KCl m/1	0·00170

It will be seen that, whereas sodium chloride has a considerable retarding effect on the rate of reaction, the action of potassium chloride is slight, and that of the nitrates negligible.

The probable mechanism of the reaction is discussed in connexion with the corresponding reaction with sodium hydroxide (p. 471).

Hydrolysis of Sodium Chloroacetate by Sodium Hydroxide.—Schwab (*loc. cit.*) has shown that in dilute solution the hydrolytic decomposition of sodium chloroacetate by sodium hydroxide is a bimolecular reaction, but that with different initial concentrations the constants decrease with dilution until about 1/20 molar solution is reached, beyond which point they remain constant. My observations, carried out at 102°, are in satisfactory agreement with those of Schwab, except that my absolute values are somewhat lower. Whilst Schwab obtains 0·163 for $k=1/c_0t\ a/a-x$ where c_0 represents the concentration, t the time in minutes, and a and $a-x$ the titration equivalents of the alkali at the commencement of the experiment and at the time t respectively (the salt and hydroxide being used in equivalent solution), I find that, when account is taken of the expansion of the solution and consequently slightly diminished concentration on heating to 102°, $k = 0{\cdot}176$ at the latter temperature. The results are summarised in the accompanying table; owing to the great speed of the reaction at 102°, the investigation of solutions above 0·2 molar is impracticable:

TABLE VII.—Temperature 102°.

Concentration.	k.	Concentration.	k.
0·2 molar	0·193	0·05 molar	0·170
0·1 ,,	0·176	0·025 ,,	0·168

With the object of determining whether the rate of hydrolysis depends on the nature of the base, comparative experiments were made with 0·1 molar solutions of sodium chloroacetate and hydroxides and potassium chloroacetate and hydroxide respectively. The mean value of the constant in the former case was 0·176 and in the latter case 0·180 (Table VIII), an agreement within the limits of experimental error, so that the hydrolysis is in all probability effected by the OH' ions.

Effect of Neutral Salts.—The influence of sodium chloride, nitrate, and sulphate and of potassium chloride and nitrate on the rate of reaction has been investigated. The results of a typical series of experiments are given in the following table, and the other results are summarised:

TABLE VIII.—Temperature 102°.

Sodium chloroacetate, 0·1 molar.
,, hydroxide, 0·1 molar.

t (min.).	$a-x$.	k.
0	37·0	—
60	18·0	0·176
180	9·0	0·173

Potassium chloroacetate, 0·1 molar.
,, hydroxide, 0·1 molar.

t (min.).	$a-x$.	k.
0	37·0	—
60	17·8	0·180
180	8·9	0·176

Sodium chloroacetate and hydroxide, 0·1 molar.
Sodium chloride, 1·0 molar.

t (min.).	$a-x$.	k.
0	37·0	—
60	15·7	0·226
180	7·5	0·219

Potassium chloroacetate and hydroxide, 0·1 molar.
Potassium chloride, 1·0 molar.

t (min.).	$a-x$.	k.
0	37·0	—
60	15·3	0·235
180	7·2	0·227

These results show that sodium and potassium chlorides accelerate the action of the respective hydroxides to exactly the same extent.

The mean value of all the observations at 102° with 0·1 molar solutions of sodium chloroacetate and hydroxide and different neutral salts are as follows:

Neutral salt ...	None	NaCl 1·0 *m*	KCl 1·0 *m*	$NaNO_3$ 1·0 *m*	Na_2SO_4 0·5 *m*
Value of k... ..	0·175	0·226	0·231	0·232	0·236

One series of observations, also with 0·1 molar solutions, was made at a much lower temperature, 48·5°, the results of which, expressed in the same units as those at the higher temperature, are appended:

Neutral salt	None	NaCl 1·0 *m*	$NaNO_3$ 1·0 *m*
Value of *k*	0·00074	0·0011	0·0012

The neutral salt action is somewhat greater at the lower temperature.

Discussion of Results.

Hydrolytic Decomposition of Sodium Chloroacetate by Water.—The question as to whether it is the undissociated salt or the chloroacetate ion which undergoes hydrolysis will first be considered. The data available for elucidating the mechanism of the change are: (1) the variation of the velocity constant with concentration (p. 468), the ratio of the rates of hydrolysis of hydrogen, sodium, and other chloroacetates; (3) the influence of neutral salts on the reaction (p. 470). As regards the first point, it has been shown that in very dilute solution the velocity is strictly proportional to the concentration, but increases more rapidly than the concentration in stronger solutions. At first sight it seems plausible to suppose that it is the undissociated salt which is being acted on. If this were the case, the degree of dissociation being smaller in the relatively stronger solutions, the increase of velocity with concentration would be accounted for, and this suggestion has actually been made by Ostwald in discussing Kastle's results. Further consideration shows, however, that this view is incompatible with the strictly unimolecular character of the change in very dilute solution, as well as with the effect of neutral salts, which in the circumstances ought to accelerate the change, whereas they exert a slight retarding effect. The comparative rates of hydrolysis of chloroacetic acid and the chloroacetates do not seem to throw much light on the question. The ratio of the velocity constants for the acid and the sodium salt in equivalent solution at the same temperature is 0·00048 : 0·00170—approximately 1 : 3·6—and this increased velocity may be accounted for either by supposing that on replacing hydrogen by sodium the resulting non-ionised salt exchanges chlorine for hydroxyl more readily than the acid does, or by assuming that the chloroacetate ion is more reactive than the non-ionised acid. The fact that barium, potassium, and sodium chloroacetates undergo hydrolysis cannot be regarded as convincing evidence that only the chloroacetate ion is being acted on in in each case. Apart from the replacement of non-ionised acid in the one case by non-ionised salt and ions in the other, the two reactions are strictly comparable, as it has been shown that neither of them is greatly affected in the first stage of decomposition by the hydrogen chloride set free.

Bearing all these facts in mind and laying most stress on the relation between reaction-velocity and concentration, the results would seem to be most readily accounted for by the view that both the undissociated salt and the chloroacetate ion undergo hydrolysis, the former about three or four more times rapidly than the latter. In strong solutions, therefore, the main reaction is expressed by the equation: $CH_2Cl\cdot CO_2Na + H_2O = OH\cdot CH_2\cdot CO_2H + HCl$, and in solutions less than *N*/10, by the equation: $CH_2Cl\cdot CO_2' + H_2O = OH\cdot CH_2\cdot CO_2' + HCl$.

The question cannot yet be regarded as finally settled and the investigation is being continued with other chloroacetates. Sodium chloroacetate reacts more rapidly than the corresponding acid with silver nitrate, and Euler (*loc. cit.*, p. 2729) considers that in the latter case it is the chloroacetate ion which is affected.

Hydrolytic Decomposition of Sodium Chloroacetate by Sodium Hydroxide.—It is of interest to compare the rates at which chloroacetic acid and its sodium salt are decomposed by water and alkali, as shown in the accompanying table:

Reacting substances	Chloroacetic acid and water	Sodium chloroacetate and water	Sodium chloroacetate and sodium hydroxide (*N*/10)
Values of *k*	0·00049	0·0017	0·0175
Comparative rates of hydrolysis ...	1	3·6	36

As the reaction velocity with sodium hydroxide was measured in *N*/10-solution, the constant in Table VIII must be divided by ten to obtain comparable values.

It appears from the above that the sodium chloroacetate is hydrolysed ten times more rapidly by *N*/10 sodium hydroxide than by water under the same conditions; the fact that in the latter case the solution becomes acid immediately hydrolysis commences does not, as we have seen, affect the reaction to a serious extent. The differences between this result and those obtained by Ostwald, Reicher, and others for the hydrolysis of esters are most striking. As is well known, methyl acetate is hydrolysed by water with extreme slowness; the reaction is greatly accelerated by the addition of dilute acids and to a much greater extent by free alkali. A comparison of the activity of alkalis and acids shows that the former are about 1000 times as effective as the latter in equivalent concentration. According to the electrolytic dissociation theory it is considered that in alkaline solution the hydroxyl ions act directly on the ester according to the typical equation, $CH_3\cdot CO_2\cdot CH_3 + OH' = CH_3\cdot CO_2' + CH_3\cdot OH$, the negative charge of the hydroxyl being transferred to the acid group. As regards the influence of acids, it is considered either that the hydrogen ions react directly with the ester, or that they accelerate the action of water on the latter, and many other examples of the catalytic action of hydrogen ions are known.

A similar explanation for the reactions described in this paper is obviously out of the question. As the product of the concentration of H′ and OH′ ions is constant, it is clear that the OH′ ion concentration in sodium chloroacetate solution (in absence of alkali) after hydrolysis has commenced is exceedingly small, and yet hydrolysis takes place with one-tenth of the rapidity observed in *N*/10 sodium hydroxide solution. Unless the improbable assumption is made that what is being measured in these cases is an isomeric transformation of the chloroacetate molecule, the results are most readily accounted for on the view that the hydrolysis of the chloroacetate is effected by undissociated water molecules, and the mechanism of the reaction may correspond with that suggested for the acid itself (p. 467).

If this suggestion is accepted, we have to account for the remarkable fact that *N*/10 alkali acts only about ten times more rapidly than water. That this is not the case in general has been proved by some preliminary experiments with monochlorohydrin,

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl,$$

which is transformed to glycerol at an enormously greater rate by alkali than by water. It might be supposed that in the former case the presence of sodium in the CO_2Na group retards the action of the corresponding hydroxide on the neighbouring CH_2Cl group; but the evidence given in this paper seems to show conclusively that it is the OH′ ion and not the non-ionised sodium hydroxide which reacts with the chloroacetate molecule. It is hoped that the investigation of other reactions will throw some light on the subject.

A comparison of Tables IV and VII shows that the deviations from the simple law of the proportionality of velocity constant and concentration are approximately the same in each instance, and, as calculation shows that they are much greater than any error due to neglecting the solution-volume of the salt, it seems justifiable to conclude that in the hydrolytic decomposition of sodium chloroacetate by water and by alkali it is the same function of the salt which is concerned in each case.

Effects of Neutral Salts on the Activity of Hydroxyl Ions.

From the table on p. 470 it is clear that the hydrolytic decomposition of sodium chloroacetate by sodium hydroxide is accelerated by all the neutral salts used, and to about the same extent. To obtain the true accelerating effect, however, it is necessary to take into account that the salts also depress the ionisation of the alkali, so that the observed velocity in the presence of neutral salts is due to a smaller concentration of OH′ ions than that in the original solution. The observations with sodium chloride and sulphate have been corrected for this effect by a method given by Arrhenius (*Zeitsch. physikal. Chem.*, 1888, 2, 284) founded on the properties of isohydric solutions, with the following results:

Composition of solution.	*K* (obs.).	*K* (corr.).	Increase per cent.
$CH_2Cl{\cdot}CO_2Na$ *m*/10 + NaOH *m*/10	0·175	0·179	—
+ *m*/1 NaCl	0·231	0·264	47
+ *m*/2 Na_2SO_4	0·236	0·260	45

These results are in striking contrast with those obtained by Arrhenius (*Zeitsch. physikal. Chem.*, 1887, 1, 110) and by Spohr (*Zeitsch. physikal. Chem.*, 1888, 2, 194) for the influence of neutral salts on the rate of hydrolysis of esters by alkali, as nearly all the salts investigated exerted a retarding effect. In none of the experiments yet made on neutral salt action, however, has it been possible to distinguish between the action on the catalyst and that on the substance acted on, and the uncertainty thus introduced is well indicated by the fact that whereas Arrhenius formerly attributed neutral salt action to an effect on the catalyst, he now considers that it is the substance acted on (sucrose) which is affected. The present investigation represents an advance in that the influence of neutral salts on the substance undergoing change has been investigated and found to be relatively small, so that it seems justifiable to ascribe the relatively large neutral salt effect in the presence of alkali to direct action of the ions of the salt on OH′ ions. The results appear to indicate that, in the absence of secondary reactions, neutral salts increase the activity of OH′ ions, just as they do that of hydrogen ions, but the further discussion of these points is postponed until the results of a more extended series of experiments now in progress are available.

The facts that sodium chloride, nitrate, and sulphate exert an equal and very considerable neutral salt action at 102°, and that, whereas neutral salts retard the action of water or sodium chloroacetate they accelerate the action of alkali on the same salt, seem to support the views on neutral salt action advanced on p. 465.

In conclusion, I wish to acknowledge the facilities for the prosecution of this work which I have enjoyed at the Davy-Faraday Research Laboratory of the Royal Institution.

XLVIII.—*New Cerium Salts.*

By GILBERT T. MORGAN and EDWARD CAHEN.

AN investigation of the thorium salts of organic acids made by one of the authors (*Pharm. J.*, 1904, October 1st, and Abstr., 1904, i, 892) showed that the aromatic sulphonates of this element are well defined, soluble, crystallisable compounds differing in this respect from the thorium salts of carboxylic acids, which, in the great majority of cases, are insoluble, amorphous substances often containing an excess of the basic radicle.

A study of the organic salts of the allied metal, cerium, has now been undertaken with the object of comparing these substances with the corresponding thorium derivatives, and also for the purpose of obtaining cerium compounds likely to be of use in the therapeutic application of this element. Hitherto only cerous oxalate has been employed in this connexion, and owing to its very sparing solubility and to the toxic action of its acid ion this salt can scarcely be regarded as a convenient medium for the exhibition of cerium.

The properties of the cerous salts of organic acids were found to resemble closely those of the corresponding thorium compounds. The cerous carboxylates, excluding those of the acetic acid series, are insoluble substances; the sulphonates are generally soluble and crystallisable. A representative group of the latter series has been prepared, and those compounds are described below. In addition to these organic sulphonates a few other cerous salts of inorganic and organic acids have been prepared in order to fill up certain gaps existing in our knowledge of cerium compounds. Cerous dichloroacetate has been obtained and compared with the corresponding acetate and mono- and tri-chloroacetates. The cerous salts of dithionic, perchloric, and nitrous acids have also been prepared.

Some special interest attaches to the nitrite, inasmuch as it affords a striking example of the colour conferring ("chromophoric") power of the nitrite ion. Cerous nitrite, a very unstable substance, separates from its yellow aqueous solution in hard, transparent, amber-yellow plates which rapidly decompose on exposure to the atmosphere; it may be preserved for a longer period in a sealed tube under dry petroleum.

The other cerous salts are either quite colourless like the perchlorate or dithionate, or exhibit at the most a very faint pink tinge such as is noticed in the case of the sulphate.

Cerous Phenol-p-*sulphonate*, $Ce_2[C_6H_4(OH)\cdot SO_3]_6,17H_2O$.

Crystallised phenol was sulphonated at 100° and the sulphonic acid converted into its barium salt, which was then recrystallised and treated with an equivalent amount of cerous sulphate, the monohydrated form, $Ce_2(SO_4)_3,H_2O$, being employed in this and the following experiments.

The filtrate from the barium sulphate was cautiously concentrated until the cerous phenol-*p*-sulphonate separated in acicular prisms or elongated lamellæ having a slightly pink tinge :

0·3018 gave 0·0646 CeO_2. Ce = 17·42.
0·3754 „ 0·0700 H_2O and 0·0792 CeO_2. H_2O = 18·64 ; Ce = 17·17.
0·3408 „ 0·2972 $BaSO_4$. S = 11·98.
$C_{36}H_{30}O_{24}S_6Ce_2,17H_2O$ requires Ce = 17·24 ; H_2O = 18·84 ; S = 11·82 per cent.

This salt dissolves readily in water, being distinctly more soluble in the cold than in the hot solvent.

The crystals separating with $17H_2O$ represent the ordinary form of the phenol-*p*-sulphonate, but a second hydrate was obtained by allowing concentrated solutions to evaporate slowly at the ordinary temperature, when long, silky needles separated. This form crystallised with 12 molecules of water :

0·3180 gave 0·0698 CeO_2. Ce = 17·86.
0·1248 „ 0·0176 H_2O and 0·0276 CeO_2. H_2O = 14·10 ; Ce = 18·00.
0·1300 „ 0·1178 $BaSO_4$. S = 12·45.
$C_{36}H_{30}O_{24}S_6Ce_2,12H_2O$ requires Ce = 18·26 ; H_2O = 14·09 ; S = 12·50 per cent.

Cerous β-Naphthol-6-*sulphonate*, $Ce_2[C_{10}H_6(OH)\cdot SO_3]_6,20H_2O$.—The barium salt of β-naphthol-6-sulphonic acid ("Schaeffer acid") was prepared by sulphonating β-naphthol with concentrated sulphuric acid (2 parts) on the water-bath, treating the product with barium carbonate, and crystallising out the less soluble constituent from the mixture of β-naphtholsulphonates. The barium β-naphthol-6-sulphonate thus obtained was treated with the requisite amount of cerous sulphate. The filtrate from the barium sulphate was evaporated on the water-bath, when the cerous salt separated in white, nacreous leaflets which are greasy to the touch:

0·1926 gave 0·0328 CeO_2. Ce = 13·87.
0·1752 „ 0·1240 $BaSO_4$. S = 9·72.
0·1192 „ 0·0218 H_2O. H_2O = 18·29.
$C_{60}H_{42}O_{24}S_6Ce_2,20H_2O$ requires Ce = 14·15 ; S = 9·70 ; H_2O = 18·20 per cent.

Cerous Camphor-β-sulphonate, $Ce_2[C_{10}H_{15}O{\cdot}SO_3]_6,20H_2O$.—This salt, which was obtained by double decomposition from barium camphor-β-sulphonate and cerous sulphate, is exceedingly soluble in water and separates from highly concentrated solutions in a mass of colourless, silky crystals; these on drying become matted together in hard, opaque nodules:

0·4396 gave 0·0762 H_2O and 0·0754 CeO_2. Ce = 13·96; H_2O = 17·34.
0·2922 „ 0·2086 $BaSO_4$. S = 9·80.
$C_{60}H_{90}O_{24}S_6Ce_2,20H_2O$ requires Ce = 13·82; H_2O = 17·76; S = 9·47 per cent.

Cerous Benzenesulphonate, $Ce_2(C_6H_5{\cdot}SO_3)_6,23H_2O$, was similarly obtained by double decomposition; it is very soluble in water and separates in lustrous, colourless, nodular crystals:

0·3594 gave 0·0928 H_2O and 0·0756 CeO_2. H_2O = 25·81; Ce = 17·12.
0·4304 „ 0·3820 $BaSO_4$. S = 12·19.
$C_{36}H_{30}O_{18}S_6Ce_2,23H_2O$ requires Ce = 17·10; H_2O = 25·30; S = 11·73 per cent.

Cerous Sulphanilate, $Ce_2[C_6H_4(NH_2){\cdot}SO_3]_6,16H_2O$, separated from aqueous solution in long, transparent, almost colourless needles, which slowly acquire a yellow tinge:

0·1448 gave 0·0312 CeO_2. Ce = 17.54.
0·1816 „ 0·0338 H_2O and 0·0386 CeO_2. H_2O = 18·61; Ce = 17·30.
0·2478 „ 0·2182 $BaSO_4$. S = 12·09.
$C_{36}H_{36}O_{18}N_6S_6Ce_2,16H_2O$ requires Ce = 17·50; H_2O = 18·00; S = 12·00 per cent.

Cerous Naphthionate, $Ce_2[C_{10}H_6(NH_2){\cdot}SO_3]_6,32H_2O$, crystallises in well-defined, mauve plates with a silvery lustre:

0·2638 gave 0·0408 CeO_2. Ce = 12·59.
0·3080 „ 0·0818 H_2O and 0·0472 CeO_2. H_2O = 26·56; Ce = 12·48.
0·3108 „ 0·1988 $BaSO_4$. S = 8·78.
$C_{60}H_{48}O_{18}N_6S_6Ce_2,32H_2O$ requires Ce = 12·76; H_2O = 26·30; S = 8·77 per cent.

Cerous Dichloroacetate, $Ce_2(CHCl_2{\cdot}CO_2)_6,3H_2O$. Barium dichloroacetate and cerous sulphate interacted to form a very soluble cerous dichloroacetate which crystallised from an aqueous solution of syrupy consistence in small nacreous leaflets:

0·1969 gave 0·0608 CeO_2. Ce = 25·12.
0·2712 „ 0·0130 H_2O and 0·0844 CeO_2. H_2O = 4·79; Ce 25·33.
0·2572 „ 0·3892 AgCl. Cl = 37·44.
$C_{12}H_6O_{12}Cl_{12}Ce_2,3H_2O$ requires Ce = 25·41; H_2O = 4·90; Cl = 38·74 per cent.

The water of crystallisation was eliminated by leaving the salt over sulphuric acid in a vacuum desiccator. This salt completes the following series, the other members having been studied by H. Wolff (*Zeitsch. anorg. Chem.*, 1905, **45**, 89):—

Cerous acetate, $Ce_2(CH_3\cdot CO_2)_6,3H_2O$. Cerous chloroacetate, $Ce_2(CH_2Cl\cdot CO_2)_6,3H_2O$. Cerous dichloroacetate,
$Ce_2(CHCl_2\cdot CO_2)_6,3HO$.
Cerous trichloroacetate, $C_2(CCl_3\cdot CO_2)_6,6H_2O$.

Cerous perchlorate, $Ce_2(ClO_4)_6,18H_2O$, prepared from barium perchlorate and cerous sulphate, is an exceedingly soluble salt which separates from very concentrated aqueous solutions in ice-like crystals which are extremely deliquescent:

0·3646 and 0·1938 gave 0·1062 and 0·0560 CeO_2. Ce = 23·71 and 23·52.

0·2228 and 0·2818 gave 0·1582 and 0·2012 AgCl. ClO_4 = 49·24 and 49·52.

0·2648 gave 0·0724 H_2O. H_2O = 27·34.

$Ce_2O_{24}Cl_6,18H_2O$ requires Ce = 23·32; ClO_4 = 49·71; H_2O = 26·98 per cent.

As the water of crystallisation is not entirely eliminated at 160°, it was estimated by decomposing the salt in a combustion apparatus and weighing the water directly. The chlorine was estimated by decomposing the perchlorate by Carius's method at 200°.

Cerous nitrite was prepared by mixing cold aqueous solutions of cerous sulphate and barium nitrite in equivalent proportions. The pale yellow solution was evaporated over caustic potash in a vacuum desiccator, when a scum of basic nitrite gradually formed and was removed by filtration. The clear yellow filtrate on further concentration deposited yellow crystals, which sometimes took the form of clear amber-coloured plates of considerable size. The substance is, however, very unstable and evolves nitrous fumes at the ordinary temperature, and, owing to the rapidity of this decomposition, it was impossible to obtain analytical numbers corresponding with the normal salt. The following data, Ce = 39·33, NO_2 = 35·38, H_2O = 26·10 (total 100·81), indicate a hydrated cerous nitrite contaminated with a certain proportion of cerous hydroxide. The salt is decomposed by warm water, nitrous fumes being evolved while the white cerous hydroxide is precipitated. Basic nitrites are obtained by adding alcohol to the concentrated solution of the normal salt. Two specimens were analysed, with the following results: (1) Ce = 52·41, NO_2 = 25·11; (2) Ce = 51·88, NO_2 = 24·93 per cent.

Cerous dithionate, $Ce_2(S_2O_6)_3,12H_2O$, was prepared from barium dithionate and cerous sulphate, the dilute filtrate being first evaporated on the water-bath, and then concentrated further in a vacuum desiccator over quicklime or caustic potash. The salt separated in colourless acicular prisms:

(*a*) 0·2904 gave 0·1033 CeO_2. Ce = 28·95.
(*b*) 0·1882 „ 0·0662 „ Ce = 28·63.
0·2900 „ 0·4124 $BaSO_4$. S = 19·53.
0·2392 „ 0·030 H_2O. H_2O = 22·16.

$Ce_2O_{18}S_6,12H_2O$ requires Ce = 28·69; S = 19·67. H_2O = 22·14 per cent.

The water was eliminated in a vacuum desiccator over sulphuric acid. Hydrates containing different proportions of water have been described, but when crystallised in the manner indicated, the salt separated with $12H_2O$. Analyses (*a*) and (*b*) were made on different preparations.

Spectroscopic Examination of the Cerous Sulphate.

The cerous sulphate employed in all the foregoing double decompositions was a specially purified sample supplied by Messrs. Hopkin and Williams; its spectroscopic examination was kindly undertaken by Mr. A. Fowler, F.R.A.S., of the Astrophysics department of the Royal College of Science, who compared its spectrum with those of the following materials also obtained from the same firm: (*a*) cerous nitrate puriss.; (*b*) commercial cerium nitrate fused; (*c*) lanthanum sulphate; (*d*) "didymium" sulphate. Mr. Fowler reports as follows:—"Photographs of the arc spectra were taken with a powerful spectrograph giving a linear dispersion of 3 tenth-metres to the millimetre in the neighbourhood of wave-length 4400. Iron was used as a reference spectrum for the determination of wave-lengths, and the spectra were also directly compared with those of lanthanum and 'didymium,' which are the chief impurities.

"The spectra are very complex, and only the part between wave-lengths 4436 and 4358 was reduced in detail. In the commercial cerium nitrate this small part of the spectrum (less than one-fortieth of the visible spectrum) yielded more than 100 lines, the identifications of which were made by reference to the tables of Exner and Haschek.

"The result of the measurements is to show that while 41 of the lines in the region investigated are due to cerium, the commercial nitrate gives strong indications of lanthanum, neodymium, praseodymium, and samarium; there are, moreover, less marked indications of gadolinium, and yttrium is somewhat doubtfully represented.

"The 'pure' nitrate and sulphate give only traces of the impurities named.

"It should be stated that there are a few lines for which no satisfactory origins can be assigned from existing tables, but there is evidence that some of these lines may be unrecorded faint lines forming part of the spectrum of cerium itself."

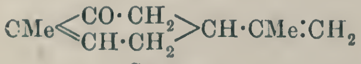
Royal College of Science, London,
South Kensington, S.W.

XLIX.—*Experiments on the Synthesis of the Terpenes. Part X. Synthesis of Carvestrene and its Derivatives.*

By William Henry Perkin, jun., and George Tattersall.

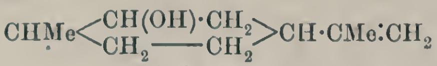
Among the many remarkable molecular changes which have so frequently been met with in the camphor and terpene group, few are more interesting and instructive than the series of decompositions which Baeyer investigated during the course of his classical researches on carvone and which, besides other important results, ultimately led to the discovery of carvestrene.

When carvone, $C_{10}H_{14}O$, a substance which occurs in oil of carraway, is reduced by sodium and alcohol, it is converted into *dihydrocarveol*, and this, on oxidation with chromic acid, yields *dihydrocarvone*,



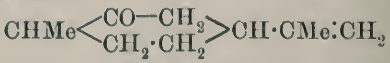
$$CMe{\leqslant}\begin{matrix}CO\cdot CH_2\\ CH\cdot CH_2\end{matrix}{>}CH\cdot CMe{:}CH_2$$

Carvone.



$$CHMe{<}\begin{matrix}CH(OH)\cdot CH_2\\ CH_2\text{——}CH_2\end{matrix}{>}CH\cdot CMe{:}CH_2$$

Dihydrocarveol.

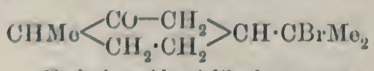


$$CHMe{<}\begin{matrix}CO\text{—}CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CMe{:}CH_2$$

Dihydrocarvone.

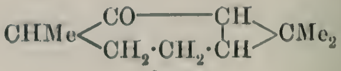
Leuckart (*Ber.*, 1887, 20, 114), Wallach (*Annalen*, 1893, 275, 110), Baeyer (*Ber.*, 1893, 26, 823).

Hydrobromic acid converts dihydrocarvone into a hydrobromide, $C_{10}H_{17}OBr$, which, when treated with alcoholic potash at 0°, readily loses hydrogen bromide. Instead, however, of the unsaturated substance, dihydrocarvone, being regenerated as the result of this decomposition, a remarkable formation of a trimethylene ring takes place and *carone* is produced.



$$CHMe{<}\begin{matrix}CO\text{—}CH_2\\ CH_2\cdot CH_2\end{matrix}{>}CH\cdot CBrMe_2$$

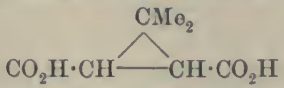
Hydrobromide of dihydrocarvone.



$$CHMe{<}\begin{matrix}CO\text{———}CH\\ CH_2\cdot CH_2\cdot CH\end{matrix}{>}CMe_2$$

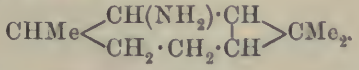
Carone.

In order to demonstrate the presence of the dimethyltrimethylene ring in carone, Baeyer and Ipatieff (*Ber.*, 1896, **29**, 2796) studied the behaviour of this ketone on oxidation with permanganate and succeeded in isolating the *cis*- and *trans*-caronic acids,



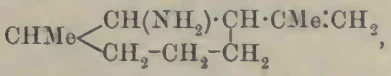
The subsequent synthesis of these acids by Perkin and Thorpe (Trans., 1899, **75**, 48), by a method which left no doubt as to their constitutions, afforded additional evidence of the presence of the dimethyltrimethylene ring in carone.

When caroneoxime is reduced by sodium and alcohol it yields *carylamine*, $C_{10}H_{17}NH_2$, and since this base is stable to permanganate, Baeyer (*Ber.*, 1894, **27**, 3486) concluded that it could not be unsaturated and must, therefore, still contain the dimethyltrimethylene ring. The constitution of carylamine is for this reason derived from that of caroneoxime in a simple manner without molecular change and is represented by the formula:



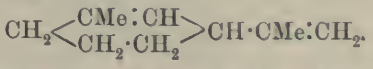
$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH(NH_2)\cdot CH}\\ \mathrm{CH_2\cdot CH_2\cdot CH}\end{matrix}>\mathrm{CMe_2}.$$

The most characteristic property of carylamine is the decomposition which it undergoes when its solution in dilute acids is evaporated, during which process the dimethyltrimethylene ring suffers disruption and the unsaturated isomeric base, *vestrylamine*,



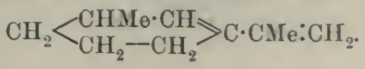
$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH(NH_2)\cdot CH\cdot CMe{:}CH_2}\\ \mathrm{CH_2{-}CH_2{-}CH_2}\end{matrix},$$

is formed. Lastly, the hydrochloride of vestrylamine is readily decomposed on distillation, with elimination of ammonium chloride and formation of *carvestrene*, an inactive terpene to which Baeyer (*loc. cit.*, 3485) assigned the constitution:



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe{:}CH_2}.$$

This formula represents carvestrene as a derivative of *m*-cymene, and direct evidence in favour of this view was subsequently obtained by Baeyer (*Ber.*, 1898, **31**, 1402), who showed that, when carvestrene dihydrobromide is treated with excess of bromine and the product reduced by zinc dust and alcoholic hydrochloric acid, it actually yields *m*-cymene. The position of the double linking in the above formula for carvestrene is rendered probable by the fact that it is formed from vestrylamine by the simple elimination of ammonia, but this decomposition might equally well lead to the expression:

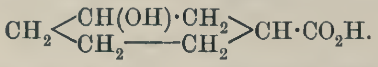


$$\mathrm{CH_2}<\begin{matrix}\mathrm{CHMe\cdot CH}\\ \mathrm{CH_2{-}CH_2}\end{matrix}>\mathrm{C\cdot CMe{:}CH_2}.$$

The properties of carvestrene which are of special importance in connexion with the present investigation are these: It distils at 178°, yields a *dihydrochloride*, $C_{10}H_{16},2HCl$, which melts at 52·5°, and a *dihydrobromide*, $C_{10}H_{16},2HBr$,* of melting point 48—50°, and gives a deep blue coloration when a drop of sulphuric acid is added to its solution in acetic anhydride.

Carvestrene occupies the same position in the *m*-cymene group of terpenes as dipentene does in the *p*-cymene series and, for this reason, it is to be considered as one of the most important of the terpenes. It therefore seemed interesting to institute a series of experiments with the object of preparing it synthetically by some process which would leave no doubt as to the constitution of the terpene, and in this we were ultimately successful.

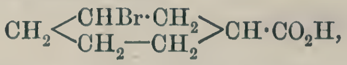
The starting point in this synthesis was *m*-hydroxybenzoic acid, which is reduced by sodium and alcohol to cyclo*hexanol*-3-*carboxylic acid*:



$$CH_2\Big<\begin{array}{c}CH(OH)\cdot CH_2\\ CH_2\text{———}CH_2\end{array}\Big>CH\cdot CO_2H.$$

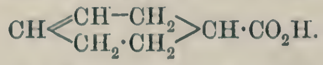
In the first place we carefully investigated this interesting acid and found that it exists in well-defined *cis*- and *trans*-modifications, of which the former (m. p. 132°) had already been obtained by Einhorn (*Annalen*, 1896, 291, 298). The *trans*-acid melts at 120°, or considerably lower than the *cis*-modification.

The *cis*-acid yields a crystalline lactone which reacts readily with hydrobromic acid with formation of the *cis*-modification (m. p. 63°) of 3-*bromo*cyclo*hexanecarboxylic acid*,



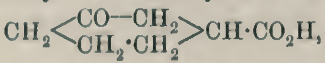
$$CH_2\Big<\begin{array}{c}CHBr\cdot CH_2\\ CH_2\text{—}CH_2\end{array}\Big>CH\cdot CO_2H,$$

whereas the *trans*-hydroxy-acid is converted, by treatment with hydrobromic acid, into the corresponding *trans*-bromo-acid of melting point 167°. When the latter is digested with diethylaniline, it is decomposed apparently quantitatively, with elimination of hydrogen bromide and formation of Δ^3-cyclo*hexenecarboxylic acid* (Δ^3-tetrahydrobenzoic acid):



$$CH\Big\langle\!\!\Big\langle\begin{array}{c}CH\text{—}CH_2\\ CH_2\cdot CH_2\end{array}\Big>CH\cdot CO_2H.$$

The second step in the synthesis of carvestrene was the conversion of *cyclo*hexanol-3-carboxylic acid into cyclo*hexanone*-3-*carboxylic acid*,



$$CH_2\Big<\begin{array}{c}CO\text{—}CH_2\\ CH_2\cdot CH_2\end{array}\Big>CH\cdot CO_2H,$$

by oxidation with chromic acid mixture, and in this way we have prepared large quantities of this important acid in a crystalline condition

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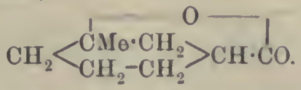
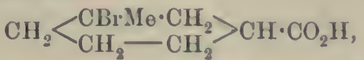
* The product of the action of hydrobromic acid on carvestrene consists of this solid dihydrobromide and a liquid isomeride, and these, doubtless, represent *cis*- and *trans*-modifications.

(m. p. 76°), whereas it had previously only been obtained as a syrup. *Ethyl* cyclo*hexanone-3-carboxylate* (b. p. 138° under 18 mm.) reacts readily with magnesium methyl iodide, and the product yields, on hydrolysis, *methyl*cyclo*hexanol-3-carboxylic acid* and a considerable quantity of an interesting neutral oil (B) the composition of which is discussed later (p. 485). The hydroxy-acid is decomposed by distillation under reduced pressure with elimination of water and formation of the lactone of *cis*-1-methyl-1-*cyclo*hexanol-3-carboxylic acid (b. p. 145° under 20 mm.):



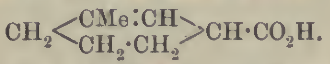
$$\begin{array}{c}\overbrace{\hphantom{\mathrm{CMe\cdot CH_2>CH\cdot C}}}^{\mathrm{O}}\\ \mathrm{CH_2}<\begin{array}{l}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2-CH_2}\end{array}>\mathrm{CH\cdot CO}.\end{array}$$

Hydrobromic acid converts this lactone into *cis*-1-*bromo*-1-*methyl*-cyclo*hexane-3-carboxylic acid*,



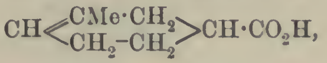
$$\mathrm{CH_2}<\begin{array}{l}\mathrm{CBrMe\cdot CH_2}\\ \mathrm{CH_2—CH_2}\end{array}>\mathrm{CH\cdot CO_2H},$$

a thick syrup which, when digested with pyridine, is decomposed with elimination of hydrogen bromide and formation of 1-*methyl*-Δ^1-cyclo*hexene-3-carboxylic acid* (b. p. 142° under 20 mm.),



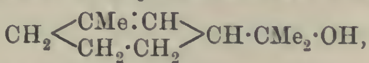
$$\mathrm{CH_2}<\begin{array}{l}\mathrm{CMe{:}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{CH\cdot CO_2H}.$$

The constitution of this acid was controlled by oxidation first with permanganate and then with chromic acid, when it yielded adipic acid and a syrupy ketonic acid which was probably ω-acetylvaleric acid, since, when treated with sodium hypobromite, it yielded bromoform and adipic acid. The formation of these oxidation products leaves no doubt that the unsaturated acid is 1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid, since the only other unsaturated acid which could result from the elimination of hydrogen bromide from 1-bromo-1-methyl*cyclo*hexane-3-carboxylic acid is 1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid,



$$\mathrm{CH}\lessdot\begin{array}{l}\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2-CH_2}\end{array}>\mathrm{CH\cdot CO_2H},$$

and an acid of this constitution could not yield adipic acid on oxidation. The 1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid was next converted into its ethyl ester (b. p. 128° under 60 mm.) and this was treated with an ethereal solution of magnesium methyl iodide, a decomposition which resulted in the synthesis of *dihydrocarvestrenol* or Δ^1-m-*menthenol* (8),



$$\mathrm{CH_2}<\begin{array}{l}\mathrm{CMe{:}CH}\\ \mathrm{CH_2\cdot CH_2}\end{array}>\mathrm{CH\cdot CMe_2\cdot OH},$$

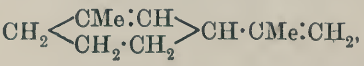
a substance which had not previously been obtained.

Dihydrocarvestrenol is a colourless syrup which distils at 105—108° (30 mm.), has a powerful odour of menthol and terpineol, and is a substance of much interest since it is the alcohol in the *m*-cymene series which corresponds to terpineol, with which, indeed, it has many properties in common. It was prepared in considerable quantity in order that its physical properties might be investigated by Sir W. H. Perkin, and an account of these experiments is to be found on p. 499. The next step was to convert the dihydrocarvestrenol into the terpene, and this was readily accomplished, in the usual manner, by digesting with potassium hydrogen sulphate, and a careful examination of the hydrocarbon obtained proved conclusively that it was in all respects identical with the carvestrene of Baeyer.

This point was decided by a direct comparison which was rendered possible by the kindness of Prof. von Baeyer, who placed his specimen of carvestrene at our disposal for this purpose.

Both preparations gave exactly the same blue coloration when sulphuric acid was added to their solution in acetic anhydride.

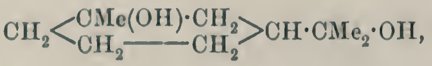
Both yielded a *dihydrochloride* melting at 52·5° and a *dihydrobromide* melting at 48—50°; moreover, the mixture of the two specimens of the dihydrobromide melted sharply at 48—50°, proving conclusively that they were identical. This synthesis establishes the constitution of carvestrene and demonstrates that the double linking in the ring is in the position assigned to it by Baeyer when he adopted the formula



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe{:}CH_2},$$

as representing the probable constitution of this terpene.

In possession of sufficient quantities of dihydrocarvestrenol and carvestrene, we instituted a series of experiments with the object of preparing the *cis-* and *trans*-modifications of *tetrahydrocarvestrenediol* (m-*menthane*-1 : 8-*diol*), $C_{10}H_{18}(OH)_2$, which it was thought would be of special interest on account of their similarity in constitution and relationship to the *cis-* and *trans*-modifications of terpin. With this object in view, dihydrocarvestrenol was shaken for several days with 5 per cent. sulphuric acid, when it was converted, almost quantitatively, into a tetrahydrocarvestrenediol,



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CMe(OH)\cdot CH_2}\\ \mathrm{CH_2 \text{———} CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH},$$

which melts at about 90°. This is the *cis*-modification and corresponds to *cis*-terpin, from which it, however, differs in being much more soluble in water and in not combining with water to form a hydrate.

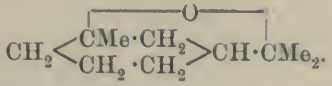
In other respects the two substances have much in common. *cis*-Tetrahydrocarvestrenediol, for example, is converted by hydrobromic acid into a mixture of the *cis-* and *trans*-carvestrene dihydrobromides, the *trans*-modification largely predominating just as, in the case of *cis*-terpin, the product of the action of hydrobromic acid in the cold consists principally of *trans*-dipentene dihydrobromide.

trans-Tetrahydrocarvestrenediol (m. p. 127°) was first prepared by Baeyer (*Ber.*, 1894, 27, 3490) from *trans*-carvestrene dihydrobromide (m. p. 48—50°) by treatment with silver acetate and subsequent hydrolysis of the diacetate produced, by alcoholic potash; a process exactly similar to the conversion of *trans*-dipentene dihydrobromide into *trans*-terpin. We have also prepared *trans*-tetrahydrocarvestrenediol and observed the same melting point, and the chief difference between *trans*-dihydrocarvestrenol and *trans*-terpin lies again in the fact that the former dissolves easily whereas the latter is sparingly soluble in water.

Direct Synthesis of Dihydrocarvestrenol [Δ^1-m-*menthenol*(8)], *Tetrahydrocarvestrenediol* (m-*menthane*-1 : 8-*diol*) *and its Anhydride* (m-*Cineol*) *from Ethyl* cyclo*Hexanone-3-carboxylate.*

It has already been mentioned that a considerable quantity of a neutral oil (B) is formed when magnesium methyl iodide reacts with ethyl *cyclo*hexanone-3-carboxylate, and examination has shown that this oil consists essentially of three substances.

I. A substance which distils at 177—178° and corresponds in the *m*-cymene series with *cineol* in the *p*-series, that is to say, it has the constitution



$$CH_2<\begin{matrix}CMe\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CMe_2.\quad (\text{O bridging } CMe \text{ and } CMe_2)$$

This interesting substance, which we have named m-*cineol*, is the anhydride of tetrahydrocarvestrenediol, and is probably formed by the dehydrating action of magnesium methyl iodide on *cis*-tetrahydrocarvestrenediol, which is doubtless one of the products of the action of this reagent on ethyl *cyclo*hexanone-3-carboxylate (see below). It has a pungent odour of camphor and is very similar to cineol in its properties, thus when treated with hydrobromic acid it is converted into a mixture of the *cis*- and *trans*-modifications of carvestrene dihydrobromide in which the *cis*-modification greatly predominates, just as cineol under the same conditions yields principally *cis*-dipentene dihydrobromide.

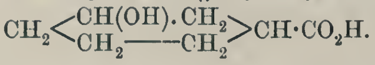
II. A substance distilling constantly at 105—108° (30 mm.) and which amounted to nearly half of the neutral oil. This substance was found to be pure *dihydrocarvestrenol*.

III. A crystalline substance melting at 127°, which was found by direct comparison to be identical with the *trans*-tetrahydrocarvestrenediol obtained from *trans*-carvestrene dihydrobromide by the process just described.

It seems probable that one of the products of the action of magnesium methyl iodide on ethyl *cyclo*hexanone-3-carboxylate is a mixture of the *cis*- and *trans*-modifications of tetrahydrocarvestrenediol, and that the *cis*-modification is then converted, by the further action of the reagent, into *m*-cineol, whereas the *trans*-modification remains unchanged.

In the communication preceding the present one, it was pointed out that *cis*-terpin is a direct product of the action of magnesium methyl iodide on ethyl *cyclo*hexanone-4-carboxylate, and the fact that it was found possible to isolate *cis*-terpin in such considerable quantities from the product of the reaction seems to indicate that this substance is not so readily converted into its anhydride, cineol, as *cis*-tetrahydrocarvestrenediol into *m*-cineol.

cis-cyclo-*Hexanol-3-carboxylic Acid* (γ-*Hydroxyhexahydrobenzoic acid*),



$$CH_2<\begin{matrix}CH(OH).CH_2\\ CH_2\text{——}CH_2\end{matrix}>CH\cdot CO_2H.$$

The reduction of *m*-hydroxybenzoic acid to *cyclo*hexanol-3-carboxylic acid by means of sodium and alcohol was first carried out by Einhorn (*Annalen*, 1896, **291**, 298), but as the process which he describes is very laborious and we required large quantities of the hexahydro-acid, we instituted a number of comparative experiments which led us to adopt the following method for its preparation.

m-Hydroxybenzoic acid (40 grams) is dissolved in absolute alcohol (1 litre), the solution heated to boiling in a large flask connected with a long reflux condenser, and then sodium (150 grams) added as rapidly as possible. When the action slackens small quantities of alcohol are added from time to time, and the heating is continued until the sodium has completely dissolved. The product is mixed with water, nearly neutralised with hydrochloric acid and evaporated until all the alcohol has been removed and sodium chloride commences to separate. The mass is then mixed with excess of hydrochloric acid and extracted ten times with washed ether, and afterwards ten times on the shaking machine, and even then the whole of the hydroxy-acid will not have been extracted. The ethereal solution is dried over calcium chloride, and nearly all the ether removed by evaporation, when, after a few days, the syrupy residue will have become semi-solid. The crystals are collected, washed with ether and recrystallised from dry ether from which cis-cyclo*hexanol-3-carboxylic acid* separates in hard crusts melting at 130—132°:

0·1241 gave 0·2648 CO_2 and 0·0936 H_2O. C = 58·2 ; H = 8·4.
$C_7H_{12}O_3$ requires C = 58·3 ; H = 8·3 per cent.

The mother liquors of the crystalline hydroxy-acid are best purified by conversion into the ester, the syrup (60 grams) being dissolved in a 4 per cent. solution of hydrogen chloride in alcohol (200 c.c.) and allowed to remain for twenty-four hours. After boiling for four hours, water is added, the crude ester extracted with ether, the ethereal solution washed with water and dilute sodium carbonate,* evaporated, and the oil fractionated under 35 mm. pressure. It began to boil at 120°, and a large fraction was obtained between this and 140,† then the ester of the hydroxy-acid distilled between 148—155° leaving a considerable quantity of a viscid residue in the flask. When the latter fraction was redistilled almost the whole quantity passed over at 147° (20 mm.) and consisted of pure *ethyl* cyclo*hexanol-3-carboxylate* :

0·1698 gave 0·3930 CO_2 and 0·1405 H_2O. C = 63·1 ; H = 9·2.
$C_9H_{16}O_3$ requires C = 62·8 ; H = 9·3 per cent.

Einhorn (*Annalen*, 1896, **291**, 301), who first prepared this substance, states that it boils at about 148—158° under 20 mm. pressure.

The results of hydrolysis indicate that this ester is a mixture of the *cis*- and *trans* modifications, the former largely predominating.

The ester (200 grams) was mixed with a warm solution of potash (100 grams) in methyl alcohol when the temperature rose to the boiling point, and, after remaining for two hours, water was added, the solution evaporated until free from methyl alcohol, acidified, saturated with ammonium sulphate, and repeatedly extracted with washed ether. The ethereal extract, after drying over calcium chloride and evaporating, deposited a syrup which soon became semi-solid, and, after remaining for several days, the mass was filtered and washed several times with pure ether, when a colourless crystalline acid was obtained which melted at 128—130° and consisted of nearly pure *cis-cyclo*hexanol-3-carboxylic acid.

The mother liquor was evaporated and the residue allowed to crystallise, and this operation repeated until the syrupy acid either did not crystallise at all or only after very long standing ; it was then treated as explained in the next section.

---

* When evaporated and heated with alcoholic hydrogen chloride, this sodium carbonate extract yields a further quantity of hydroxy-ester.

† When this fraction was twice distilled under the ordinary pressure, almost the whole quantity came over at 200—202° and gave, on analysis :

0·1711 gave 0·4377 CO_2 and 0·1447 H_2O C = 69·8 ; H = 9·5.
$C_9H_{14}O_2$ requires C = 70·1 ; H = 9·1 per cent.

It is evident that this substance is the ester of one of the tetrahydrobenzoic acids, and, as a large quantity has accumulated, it will be further investigated.

The Lactone of cis-cyclo*Hexanol-3-carboxylic Acid and its Conversion into* cis-3-*Bromo*cyclo*hexanecarboxylic Acid.*

When the uncrystallisable hydroxy-acid, obtained as explained in the last section, is slowly distilled under a pressure of 30 mm., water is eliminated, and an oil passes over at 125—140° which becomes semi-solid on cooling. The thermometer then rises rapidly to 180°, between which temperature and 195° a large amount of a colourless oil (A) distils and also solidifies on cooling. The lower fraction was redistilled, when a considerable quantity passed over at 125—130° (20 mm.) and crystallised in the condenser to a camphor-like mass. This substance, which was found to be the lactone of the *cis*-hydroxy-acid, was left in contact with porous porcelain until quite free from oil, and then crystallised from light petroleum.

0·1067 gave 0·2600 CO_2 and 0·0756 H_2O. C = 66·5; H = 7·9.

$C_7H_{10}O_2$ requires C = 66·7; H = 7·9 per cent.

The *lactone* of cis-cyclo*hexanol-3-carboxylic acid* separates from light petroleum in groups of small needles, but, even when freshly crystallised, it is of such a curious sticky nature that it was found impossible to introduce it into a capillary tube, and the quantity was too small to allow of its melting point being determined by any other process. It is insoluble in sodium carbonate in the cold, but is readily hydrolysed by methyl-alcoholic potash, and if the solution is evaporated until free from alcohol, acidified, and repeatedly extracted with ether, the ethereal solution, after drying over calcium chloride and evaporating to a small bulk, deposits colourless crusts which melt at 132°, and consist of the pure *cis*-hydroxy-acid:

0·1535 gave 0·3269 CO_2 and 0·1181 H_2O. C = 58·1; H = 8·5.

$C_7H_{12}O_3$ requires C = 58·3; H = 8·4 per cent.

The lactone dissolves in aqueous hydrobromic acid (saturated at 0°) and, on standing, crystalline crusts gradually separate. These were collected, drained on porous porcelain, rapidly washed on porous porcelain with formic acid (sp. gr. 1·22), and dried over sulphuric acid under reduced pressure:

0·2347 gave 0·2185 AgBr. Br = 38·1.

$C_7H_{11}O_2Br$ requires Br = 38·6 per cent.

Purified in this way, cis-3-*bromo*cyclo*hexanecarboxylic acid* melts at about 62—63°, and differs from the corresponding *trans*-isomeride (m. p. 167°, see p. 489) by its much lower melting point and by the fact that it is much more soluble in formic acid and other solvents.

trans-cyclo*Hexanol-3-carboxylic Acid and its Conversion into* trans-3-*Bromo*cyclo*hexanecarboxylic Acid and into* Δ^3-cyclo-*Hexenecarboxylic Acid.*

In the last section mention is made of an oil (A) which distilled at about 195° (30 mm.) and solidified on cooling, and investigation has shown that this consists of *trans-cyclo*hexanol-3-carboxylic acid. The crystalline mass was left in contact with porous porcelain until free from oil, and several times crystallised from ether, from which the new acid separated in colourless crusts:

0·1686 gave 0·3598 CO_2 and 0·1289 H_2O. C = 58·2; H = 8·5.
$C_7H_{12}O_3$ requires C = 58·3; H = 8·4 per cent.

trans-cyclo-*Hexanol-3-carboxylic acid* melts at 119—120°, and is readily soluble in water or alcohol, but very sparingly so in dry ether. In its other properties it shows great similarity to the corresponding *cis*-acid, but when it is intimately mixed with an equal quantity of the *cis*-acid (m. p. 132°) the mixture shrinks at 90° and is almost completely melted at 100°, a behaviour which clearly proves that the acids are distinct. The *trans*-acid dissolves readily in aqueous hydrobromic acid (saturated at 0°) and no separation takes place even after twenty-four hours, but when heated at 100° for a few minutes the solution separates into two layers, of which the upper is the bromo-acid. This was isolated by diluting with water and extracting with ether, and, after the ethereal solution had been well washed with water, dried over calcium chloride, and evaporated, a viscid syrup remained which soon commenced to crystallise. The crystalline mass was drained on porous porcelain and twice recrystallised from light petroleum, when crystalline crusts were obtained which gave the following results on analysis:

0·3476 gave 0·3112 AgBr. Br = 38·2.
$C_7H_{11}O_2Br$ requires Br = 38·6 per cent.

trans-3-*Bromo*cyclo*hexanecarboxylic acid* melts at 167°, and is characterised by the facility with which it crystallises from organic solvents. It dissolves readily in boiling benzene, and separates on cooling in four-sided plates with bevelled edges. It is also readily soluble in methyl alcohol, chloroform, or ethyl acetate, from all of which it crystallises beautifully.

Towards hydrobromic acid the *cis*- and *trans*-modifications of *cyclo*hexanol-3-carboxylic acid show apparently an exactly similar behaviour. The acids dissolve readily in the hydrobromic acid and no change takes place at the ordinary temperature. When the solution is heated at 100°, a thick syrup separates which consists of the *trans*-bromo-acid of melting point 167°, together with a more soluble bromo-acid of much lower melting point which is doubtless the *cis*-modification. Apparently hydrobromic acid at 100° yields, in each case, an equilibrium mixture of the two modifications of the bromo-acid.

Δ^3 cyclo*Hexenecarboxylic Acid* (Δ^3-tetrahydrobenzoic acid).—*trans*-3-Bromo*cyclo*hexanecarboxylic acid is a very stable substance, since it is only very slowly decomposed by boiling pyridine; when, however, it is digested with diethylaniline for one hour, complete decomposition takes place with elimination of hydrogen bromide and formation of Δ^3-*cyclo*hexenecarboxylic acid. The product was treated with excess of dilute hydrochloric acid, extracted with ether, the ethereal solution well washed, dried over calcium chloride, evaporated, and the residue distilled under reduced pressure, when almost the whole quantity passed over at 133° (20 mm.) and solidified readily in a freezing mixture:

0·1635 gave 0·3981 CO_2 and 0·1175 H_2O. C = 66·4; H = 8·0.

$C_7H_{10}O_2$ requires C = 66·6; H = 7·9 per cent.

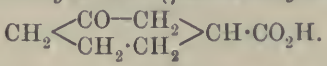
In order to prove that this substance was Δ^3-*cyclo*hexenecarboxylic acid, its behaviour towards bromine was investigated, when it was found that 4·26 grams, dissolved in chloroform and cooled to − 10°, absorbed about 5·5 grams of bromine without evolution of hydrogen bromide, but the end point was not quite sharp. The quantity of bromine which should, theoretically, have been absorbed in converting the above amount of an unsaturated acid, $C_7H_{10}O_2$, into the dibromo-addition product, $C_7H_{10}O_2Br_2$, is 5·41 grams. The product was allowed to remain on a clock glass exposed to air until almost the whole of the chloroform had evaporated, the syrupy residue was then left over sulphuric acid in contact with a crystal of 3 : 4-dibromo*cyclo*hexanecarboxylic acid, when crystallisation soon commenced. After traces of oily impurity had been removed by contact with porous porcelain, the residue was washed on porous porcelain with formic acid and recrystallised from this solvent, when colourless plates separated which melted at 86°:

0·1585 gave 0·2072 AgBr. Br = 55·6.

$C_7H_{10}O_2Br_2$ requires Br = 55·9 per cent.

That this substance was 3 : 4-dibromo*cyclo*hexanecarboxylic acid ($\gamma\delta$-dibromohexahydrobenzoic acid) was shown by mixing it with a specimen of this acid which had previously been prepared (Trans., 1904, **85**, 433) from *cyclo*hexanol-4-carboxylic acid, when no alteration in melting point could be observed.

cyclo*Hexanone-3-carboxylic Acid* (*γ-ketohexahydrobenzoic acid*),



$$CH_2<\begin{matrix}CO-CH_2\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H.$$

This acid is produced by the oxidation of *cis-cyclo*hexanol-3-carboxylic acid, and after many comparative experiments we finally adopted the following process for the preparation of the large quantities of the acid and its ester which were required for this research. The *cis*-acid * (50 grams) is dissolved in water (200 c.c.) warmed to 45°, and then a solution of potassium dichromate (70 grams) and sulphuric acid (50 c.c.) in water (300 c.c.) is added in small quantities at a time, a fresh quantity only being added after the previous one had been completely reduced. The product is cooled, saturated with ammonium sulphate and extracted at least ten times on the shaking machine; the extract is dried over calcium chloride, evaporated, and the crude acid converted at once into its ester. In doing this care must always be taken to use only weak alcoholic solutions of hydrochloric or sulphuric acids, otherwise condensation takes place with formation of oils of very high boiling point. The crude acid (20 grams) is left in contact with a 2·5 per cent. solution of alcoholic hydrogen chloride (75 c.c.) for three days and then heated to boiling for one hour. After diluting with water and extracting with ether, the ethereal solution is washed with water and dilute sodium carbonate, evaporated, and the residue fractionated several times under reduced pressure from a distilling flask with a long neck in order that the separation of the keto-ester from any unchanged hydroxy-ester may be as complete as possible:

0·2891 gave 0·6711 CO_2 and 0·2236 H_2O. C = 63·3; H = 8·6.
0·1777 ,, 0·4161 CO_2 ,, 0·1380 H_2O. C = 63·3; H = 8·7.
$C_9H_{14}O_3$ requires C = 63·5; H = 8·3 per cent.

Ethyl cyclo*hexanone-3-carboxylate* distils at 138° under 18 mm. pressure, and not at 170—180° (16 mm.) as stated by Einhorn (*Annalen*, 1896, **291**, 303).

In order to prepare the keto-acid, the pure ester was digested with dilute hydrochloric acid until solution was complete, the product was then evaporated on the water-bath until free from alcohol, saturated with ammonium sulphate, and repeatedly extracted with ether.

The ethereal solution was dried over calcium chloride, evaporated, and the residue distilled under reduced pressure (30 mm.), when almost the whole quantity passed over at 205° as a viscid, colourless oil, which gradually and almost completely crystallised. After remaining in contact with porous porcelain for some days, the acid was crystallised from benzene, from which it separates in hard crusts, or if the cold saturated solution is allowed to evaporate slowly the acid is obtained in the form of small glistening prisms:

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* In some of our experiments we oxidised the crude mixture of *cis*- and *trans*-isomerides (p. 487), but the yield of keto-acid always seemed to be much more satisfactory when the pure *cis*-acid was employed.

0·1835 gave 0·3981 CO_2 and 0·1179 H_2O. C = 59·1; H = 7·1.
0·1464 „ 0·3174 CO_2 „ 0·0936 H_2O. C = 59·2; H = 7·1.
$C_7H_{10}O_3$ requires C = 59·1; H = 7·0 per cent.

cyclo*Hexanone-3-carboxylic acid* melts at 75—76° and is very soluble in water, alcohol, or benzene, but sparingly so in light petroleum.

The *silver* salt, $C_7H_9O_3Ag$, was prepared by adding silver nitrate to a hot slightly alkaline solution of the ammonium salt when the filtered liquid, on slowly cooling, deposited the silver salt as a voluminous felted mass of minute needles:

0·3011 gave 0·1309 Ag. Ag = 43·4.
$C_7H_9O_3$ Ag requires Ag = 43·3 per cent.

This silver salt is somewhat readily soluble even in cold water. The neutral solution of the ammonium salt of the keto-acid gives no precipitate with barium or calcium chlorides, or with lead acetate or copper sulphate.

The oxime.—In order to prepare this derivative, *cyclo*hexanone-3-carboxylic acid (2 grams) was dissolved in water and mixed with a solution of hydroxylamine hydrochloride (2 grams) and caustic potash (4 grams). After twenty-four hours a slight excess of hydrochloric acid was added, the clear solution extracted ten times with ether, and the ethereal solution dried over calcium chloride and evaporated. The syrupy residue gradually crystallised, and, after draining on porous porcelain, the oxime was purified by crystallisation from ether.

0·1813 gave 13·7 c.c. nitrogen at 10° and 752 mm. N = 8·8.
$C_7H_{11}O_3N$ requires N = 8·9 per cent.

cyclo*Hexanoneoxime-3-carboxylic acid* separates from ether in hard, crystalline crusts and melts at 170° as stated by Baeyer.

It dissolves very readily in warm water and crystallises from a saturated solution, on long standing, in warty masses.

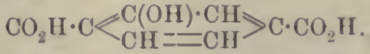
The *semicarbazone.*—When an aqueous solution of the keto-acid is mixed with semicarbazide hydrochloride and sodium acetate and allowed to stand, the semicarbazone gradually separates as a hard, crystalline crust. It is very sparingly soluble in alcohol or water, but may be crystallised from either solvent, and is thus obtained as a sandy, crystalline precipitate which melts at 182—183° with decomposition:

0·1601 gave 28·5 c.c. nitrogen at 16° and 758 mm. N = 20·9.
$C_8H_{13}O_3N_3$ requires N = 21·2 per cent.

Formation of cyclo*Hexanone-3-carboxylic Acid from Terephthalic Acid.*

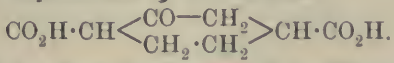
During his investigation of the reduction products of terephthalic acid, Baeyer (*Ber.*, 1889, **22**, 2178) showed that this acid may be converted into *cyclo*hexanone-3-carboxylic acid by the following interesting series of reactions.

Terephthalic acid is nitrated and the nitro-acid reduced to aminoterephthalic acid, which, when treated with sodium nitrite, yields *hydroxyterephthalic acid*,



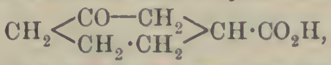
$$CO_2H\cdot C\Big<\begin{matrix}C(OH)\cdot CH\\ CH=CH\end{matrix}\Big>C\cdot CO_2H.$$

This hydroxy-acid is readily reduced by sodium amalgam with the formation of cyclo*hexanone*-3 : 6-*dicarboxylic acid*, the constitution of which is probably represented by the formula



$$CO_2H\cdot CH\Big<\begin{matrix}CO-CH_2\\ CH_2\cdot CH_2\end{matrix}\Big>CH\cdot CO_2H.$$

When this acid is warmed with water it is decomposed with evolution of carbon dioxide and formation of cyclo*hexanone*-3-*carboxylic acid*,



$$CH_2\Big<\begin{matrix}CO-CH_2\\ CH_2\cdot CH_2\end{matrix}\Big>CH\cdot CO_2H,$$

which was obtained as a syrup, but was characterised by conversion into the oxime, which melted at 170° (compare p. 492).

When we commenced the present research, this series of decompositions, discovered by Baeyer, was very carefully investigated, because it seemed possible that this process might prove to be the simplest method for the preparation of the large quantities of *cyclo*hexanone-3-carboxylic acid which we required for our synthetical experiments. We therefore prepared a large amount of hydroxyterephthalic acid, and carefully purified it by converting it into its methyl ester, which, after crystallisation from methyl alcohol, melted at 96° :

0·1956 gave 0·4093 CO_2 and 0·0829 H_2O. $C=57·0$; $H=4·7$.
$C_{10}H_{10}O_5$ requires $C=57·1$; $H=4·8$ per cent.

This ester was hydrolysed, reduced by sodium amalgam, and the *cyclo*hexanone-3 : 6-dicarboxylic acid, isolated in the manner recommended by Baeyer, was obtained in the form of pale yellow crusts which gave correct numbers on analysis :

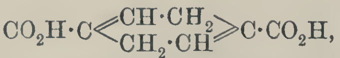
0·1505 gave 0·2848 CO_2 and 0·0781 H_2O. $C=51·7$; $H=5·7$.
$C_8H_{10}O_5$ requires $C=51·6$; $H=5·4$ per cent.

When this acid was boiled with water, carbon dioxide was slowly eliminated, and the solution, on standing, deposited a considerable quantity of a very sparingly soluble acid. This was collected and purified by recrystallisation from glacial acetic acid, from which it separated as a pale ochre, granular, crystalline mass.

Two different specimens gave the following results on analysis:

0·1577 gave 0·3286 CO_2 and 0·0645 H_2O. C = 56·8; H = 4·6.
0·1735 „ 0·3624 CO_2 „ 0·0736 H_2O. C = 56·9; H = 4·7.
$C_8H_8O_4$ requires C = 57·1; H = 4·8 per cent.

The investigation of this acid has proved conclusively that it is $\Delta^{1:4}$-cyclo*hexadiene*-1:4-*dicarboxylic acid* ($\Delta^{1:4}$-dihydroterephthalic acid),



$$\mathrm{CO_2H\cdot C}\left<\begin{array}{l}\mathrm{CH\cdot CH_2}\\ \mathrm{CH_2\cdot CH}\end{array}\right>\mathrm{C\cdot CO_2H},$$

and had evidently been formed by the elimination of water from *cyclo*hexanone-3:6-dicarboxylic acid during the boiling with water.

This acid was obtained by Baeyer (*Annalen*, 1888, **245**, 145; 1889, **251**, 272), by the direct reduction of terephthalic acid with sodium amalgam. It gives a dimethyl ester of melting point 130°, which is characterised by yielding an intense yellow colour when its alcoholic solution is warmed with alcoholic potash, and these properties were also exhibited by the acid obtained by us.

The aqueous solution, from which the *cyclo*hexadiene-1:4-dicarboxylic acid had been separated, was saturated with ammonium sulphate and extracted twenty times with ether, when the ethereal solution, after drying over calcium chloride and evaporating, deposited, as Baeyer describes, a syrupy acid which yielded an oxime of melting point 170°, and obviously consisted of impure *cyclo*hexanone-3-carboxylic acid.

This crude acid distilled with considerable decomposition even under low pressures; it was therefore converted into its ester (compare p. 491), and this, on distillation under 18 mm. pressure, yielded a quantity of oil boiling at 135—145°, but there was a considerable amount of an oil of higher boiling point left in the flask.

When this oil was hydrolysed, a syrupy acid was obtained which distilled at about 205° (30 mm.) and gradually solidified; after crystallisation from benzene, the hard crusts melted at 76° and were found, by direct comparison, to be identical with *cyclo*hexanone-3-carboxylic acid (p. 492).

0·1317 gave 0·2854 CO_2 and 0·0845 H_2O. C = 59·1; H = 7·2.
$C_7H_{10}O_3$ requires C = 59·1; H = 7·0 per cent.

These experiments clearly indicated that the above process was not suitable for preparing *cyclo*hexanone-3-carboxylic acid in quantity, and it was therefore abandoned in favour of the method of preparation described on p. 491.

The Lactone of cis-1-*Methyl*cyclo*hexanol-3-carboxylic Acid* (cis-γ-Hydroxyhexahydro-*m*-toluic Acid) *and its Conversion into* cis-1-*Bromo*-1-*methyl*cyclo*hexane-3-carboxylic Acid.*

When ethyl *cyclo*hexanone-3-carboxylate (50 grams) is gradually added to an ethereal solution of magnesium methyl iodide (containing 15 grams of magnesium) a vigorous action takes place which must be moderated by cooling in ice water, and a thick, oily layer separates which gradually crystallises. After remaining overnight, the product is decomposed with dilute hydrochloric acid in the usual manner, extracted at least twenty times with ether on the shaking machine, the ethereal solution evaporated, and the residue (45 grams) digested for one hour with potash (50 grams) dissolved in methyl alcohol. Water is then added, the neutral oil (B, 10 grams, see p. 502) extracted several times with ether, the alkaline solution neutralised, evaporated until free from alcohol, acidified, and extracted many times with ether. The ethereal solution is dried over calcium chloride and evaporated, and the thick, syrupy methylhydroxy-acid converted into the lactone by distillation under reduced pressure (20 mm.).

At first much water is given off, and then about two-thirds distils at 130—150°, but a considerable fraction, 180—200°, is also obtained, which probably contains the *trans*-methylhydroxy-acid, and a thick residue remains in the flask. The distillate is dissolved in ether dried over calcium chloride and again several times fractionated, when the lactone (15—20 grams) is readily obtained pure:

0·1933 gave 0·4844 CO_2 and 0·1504 H_2O. C = 68·3; H = 8·6.

0·1543 „ 0·3881 CO_2 „ 0·1201 H_2O. C = 68·6; H = 8·6.

$C_8H_{12}O_2$ requires C = 68·6; H = 8·6 per cent.

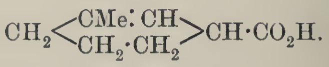
The lactone of cis-1-*methyl*cyclo*hexanol-3-carboxylic acid* is a colourless oil which distils at 145° (20 mm.) and at 170—171° (100 mm.).

In order to prepare cis 1-*bromo*-1-*methyl*cyclo*hexane-3-carboxylic acid*, the lactone (10 grams) is dissolved in aqueous hydrobromic acid (saturated at 0°, 20 c.c.), when an oil soon separates, and, after remaining for twenty-four hours, water is added, the heavy oily layer extracted with ether, dried over calcium chloride, and evaporated. The residual, almost colourless syrup did not crystallise, but after remaining for twelve hours in an evacuated desiccator, it yielded analytical results which agree approximately with those required for the bromo-acid:

0·1715 gave 0·1421 AgBr. Br = 35·3.

$C_8H_{13}O_2Br$ requires Br = 36·2 per cent.

1-*Methyl*-Δ^1-cyclo*hexene-3-carboxylic Acid*,



$$CH_2<\begin{matrix}CMe:CH\\ CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2H.$$

In the preparation of this acid, 1-bromo-1-methyl*cyclo*hexane-3-carboxylic acid was dissolved in anhydrous pyridine (3 vols.) and heated on the water-bath for two hours, when crystals of pyridine hydrobromide separated in quantity. After heating to boiling for ten minutes, the mass was mixed with water and distilled in steam, the distillate was acidified with hydrochloric acid, extracted with ether, and the ethereal solution dried over calcium chloride and evaporated. The residue distilled almost constantly at 140—142° (20 mm.), but the unsaturated acid was nevertheless not quite pure, since it dissolved in sodium carbonate, yielding an opalescent solution, a behaviour probably due to the presence of traces of lactone, and it also contained traces of bromine:

0·2055 gave 0·5113 CO_2 and 0·1588 H_2O. $C = 67·7$; $H = 8·6$.
0·1438 „ 0·3588 CO_2 „ 0·1137 H_2O. $C = 68·0$; $H = 8·6$.
$C_8H_{12}O_2$ requires $C = 68·6$; $H = 8·6$ per cent.

1-*Methyl*-Δ^1-cyclo*hexene-3-carboxylic acid* is a colourless oil which does not crystallise when cooled to $-10°$; it shows the behaviour of an unsaturated acid, since it decolorises bromine, and its solution in sodium carbonate instantly reduces permanganate.

In order to determine whether this acid was a single substance or a mixture, a considerable quantity was converted into the calcium salt by boiling with water and an excess of freshly precipitated calcium carbonate. The solution was concentrated and five crops of calcium salt were collected, but no difference in the appearance of the crops could be detected. They were all analysed and found to contain the same percentage of water of crystallisation and of calcium, and it will be only necessary to give details of the analyses of Crops I and V in illustration of this point:

Crop I.—0·4201, heated at 100°, lost 0·0879 H_2O and yielded 0·1369 $CaSO_4$. $H_2O = 20·9$; $Ca = 9·6$.

Crop V.—0·4532, heated at 100°, lost 0·0948 H_2O and yielded 0·1514 $CaSO_4$. $H_2O = 20·8$; $Ca = 9·7$.

$C_{16}H_{22}O_4Ca,5H_2O$ requires $H_2O = 22·0$; $Ca = 9·8$ per cent.

These results indicate that the unsaturated acid, prepared as explained above, is a single substance. In order to determine the position of the double linking in this acid, its behaviour on oxidation was next investigated.

In carrying out this experiment, the acid (15 grams) was dissolved in dilute sodium carbonate, and, after mixing with powdered ice, a 1 per cent. solution of potassium permanganate was slowly run in until the colour remained, carbon dioxide being passed through and the liquid well stirred with a turbine during the operation. The excess of permanganate was destroyed by the addition of sodium sulphite, the product heated on the water-bath, filtered, and the filtrate and washings of the manganese precipitate evaporated to a small bulk. After acidifying with hydrochloric acid, saturating with ammonium sulphate, and extracting twenty times * with ether on the shaking machine, a viscid oil (12 grams) was obtained which had a strong odour of acetic acid and did not crystallise. This was dissolved in water, warmed to 60°, and a dilute solution of sodium dichromate and sulphuric acid gradually added until the oxidation was complete. After saturating with ammonium sulphate and extracting twenty times with ether, a brown oil was obtained which was converted into the ester by treating with alcohol and sulphuric acid in the usual manner. When this ester was fractionated under 20 mm. pressure, about one-third distilled at 130—140° and almost the whole of the remainder at 175—185°. The lower fraction contained ethyl adipate, since, on hydrolysis, it yielded an acid which, after crystallising from water, melted at 148° and proved to be adipic acid, because, when mixed with a specimen of pure adipic acid, no alteration in the melting point could be observed. The fraction 175—185° (20 mm.) probably contains ethyl ω-acetylvalerate, $COMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$, since, on analysis, it gave numbers agreeing approximately with this formula and showed the following behaviour. Hydrolysis with methyl-alcoholic potash yielded a syrupy acid which did not crystallise (ω-acetylvaleric acid, when quite pure, crystallises and melts at 40—42°), but which gave an immediate precipitate with *p*-bromophenylhydrazine acetate and yielded bromoform and adipic acid when it was treated with bromine and caustic potash.

Ethyl 1-*Methyl*-Δ^1-cyclo*hexene-3-carboxylate.*—In preparing this ester, the acid (25 grams) was mixed with alcohol (250 c.c.) and sulphuric acid (20 c.c.), and, after remaining for 12 hours, heated on the water-bath for half an hour. Water was then added and the ester extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride, and fractionated under reduced pressure:

0·1365 gave 0·3552 CO_2 and 0·1153 H_2O. C = 70·9 ; H = 9·4.

$C_{10}H_{12}O_2$ requires C = 71·4 ; H = 9·5 per cent.

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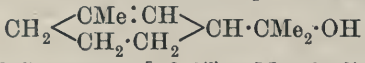
* When the fifteenth to twentieth extractions were evaporated to a small bulk, a very small quantity of a crystalline acid separated which melted at 193° and, on analysis, gave numbers agreeing with $C_8H_{16}O_4$ and also approximately with $C_8H_{14}O_4$. This acid is readily soluble in warm water, but almost insoluble in cold ether, and when heated in a test-tube, part decomposes and part sublimes unchanged and the distillate gives an immediate precipitate with *p*-bromophenylhydrazine.

Possibly this acid is one of the modifications of 1-methyl*cyclo*hexane-1 : 2-diol-3-carboxylic acid, but the amount available was too small for further investigation.

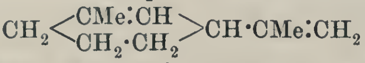
Ethyl 1-*methyl*-Δ^1-cyclo*hexene*-3-*carboxylate* distils at 128° (60 mm.) and has a very penetrating, sickly odour.

Synthesis of Dihydrocarvestrenol [Δ^1-m-*Menthenol* (8)]



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CMe:CH}\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe_2\cdot OH}$$

and Carvestrene [$\Delta^{1:8(9)}$-*m*-Menthadiene]



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CMe:CH}\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH\cdot CMe:CH_2}$$

from Ethyl 1-*Methyl*-Δ^1-cyclo*hexene*-3-*carboxylate.*

The synthesis of dihydrocarvestrenol was carried out as follows. Ethyl 1-methyl-Δ^1-*cyclo*hexene-3-carboxylate (30 grams) was gradually added to an ethereal solution of magnesium methyl iodide (containing 12 grams of magnesium), when very little evolution of heat was noticed at the time of mixing, but, on standing, the temperature gradually rose to the boiling point of the ether so that the flask had to be cooled from time to time. After remaining for twenty-four hours, the product was decomposed by water and dilute hydrochloric acid, the ethereal solution evaporated, and the residue digested for a few minutes with methyl-alcoholic potash (containing 5 grams of KOH) in order to remove any unchanged ester which might be present. The product was diluted with water, extracted with ether, and the ethereal solution, after washing with water and drying over calcium chloride, evaporated, when an almost colourless oil remained which, after two fractionations, distilled constantly at 105—108° (30 mm.):

0·1650 gave 0·4711 CO_2 and 0·1751 H_2O. $C = 77·8$; $H = 11·7$.
0·1322 ,, 0·3765 CO_2 ,, 0·1411 H_2O. $C = 77·6$; $H = 11·8$.
$C_{10}H_{18}O$ requires $C = 77·9$; $H = 11·7$ per cent.

Dihydrocarvestrenol is a viscous, colourless oil which has a penetrating odour of menthol and terpineol and, so far, has not been obtained in a crystalline condition. Its solution in acetic anhydride gives, with a drop of sulphuric acid, at first a violet coloration, but this soon changes to an intense methylene-blue.

The determination of the physical properties of dihydrocarvestrenol was undertaken by Sir W. H. Perkin, with the following results:

d 4°/4° = 0·9338; d 15°/15° = 0·9257; d 25°/25° = 0·9196.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
14·45°	1·1945	11·035

Refractive power:

$t = 15°$; $d\ 15°/4° = 0·92299$.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α.........	1·47521	0·50934	78·438
β	1·48532	0·52018	80·107
γ.........	1·49144	0·52673	81·116

Dispersion $\gamma - \alpha = 2·678$.

In order to compare these numbers with the physical properties of terpineol, a very pure sample of the latter was prepared by fractionating crystalline terpineol from Schimmel. The examination of this specimen gave the following results:

Density (surfused): $d\ 15°/15° = 0·9415$; $d\ 25°/25° = 0·9358$.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
17°	1·1951	10·876

Refractive power:

$t = 14·8°$; $d\ 14·8°/4° = 0·94080$.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α.........	1·48211	0·51244	78·916
β	1·49183	0·52278	80·508
γ.........	1·49763	0·52894	81·457

Dispersion $\gamma - \alpha = 2·541$.

It will be seen from these numbers that the similarity in physical properties between dihydrocarvestrenol and terpineol is very striking.

When dihydrocarvestrenol is mixed with an equal weight of powdered potassium hydrogen sulphate and heated to boiling in a reflux apparatus by means of an oil-bath, water is readily eliminated and *carvestrene* is formed. After boiling for half an hour, the product is treated with water to dissolve the salt, extracted with ether, the ethereal solution is washed with water, dried over calcium chloride and evaporated, and the oil distilled, when almost the whole quantity passes over at 175—185°, the conversion of the alcohol into the hydrocarbon taking place nearly quantitatively. After twice distilling over sodium, the hydrocarbon boiled constantly at 178—179° (750 mm.):

0·1449 gave 0·4658 CO_2 and 0·1568 H_2O. C = 88·7; H = 12·0.
0·1313 „ 0·4240 CO_2 „ 0·1401 H_2O. C = 88·1; H = 11·9.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

Synthetical carvestrene has a pungent odour of lemons, and its solution in acetic anhydride is coloured a deep methylene-blue when a drop of sulphuric acid is added. It oxidises in the air, but not nearly so rapidly as dipentene does. The identity of synthetical carvestrene with the hydrocarbon prepared by Baeyer (*Ber.*, 1894, **27**, 3485) from vestrylamine was proved by the preparation of the following derivatives.

Carvestrene Dihydrochloride, $C_{10}H_{16},2HCl$.—In order to prepare this characteristic derivative, synthetical carvestrene was dissolved in an equal volume of pure ether and slowly saturated with dry hydrogen chloride, the temperature being kept at − 10° during the operation.

The solution gradually became dark brown, and, after remaining over night, it was poured on a clock glass and the ether allowed to evaporate, when an oil remained which soon crystallised. In contact with porous porcelain, the dark coloured impurities were quickly absorbed and the almost colourless residue separated from methyl alcohol in needles of melting point 52·5°:

0·1988 gave 0·2711 AgCl. Cl = 33·7.

$C_{10}H_{18}Cl_2$ requires Cl = 33·9 per cent.

Carvestrene Dihydrobromide, $C_{10}H_{16},2HBr$.—In preparing this derivative a saturated solution of hydrogen bromide in acetic acid (5 c.c.) was cooled to − 10° and mixed with synthetical carvestrene (1 c.c.).

At first the hydrocarbon floated, but, after 24 hours, a heavy oil had separated below the acid, and shortly afterwards this began to crystallise. The crystals were left in contact with porous porcelain until quite free from oil (see below) and then crystallised from methyl alcohol:

0·2317 gave 0·2920 AgBr. Br = 53·6.

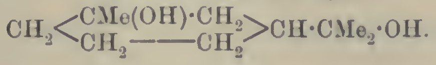
$C_{10}H_{18}Br_2$ requires Br = 53·7 per cent.

Carvestrene dihydrobromide separates from methyl alcohol in hard, prismatic needles and melts at 48—50°.

The dihydrochloride and dihydrobromide prepared from synthetical carvestrene have exactly the same melting points as the corresponding derivatives obtained by Baeyer (*Ber.*, 1894, **27**, 3490) from carvestrene from vestrylamine. Baeyer was kind enough to send the authors a small quantity of his carvestrene, which was converted into the dihydrobromide of melting point 48—50°. When this was mixed with an equal quantity of the dihydrobromide from synthetical carvestrene, no alteration in melting point could be observed, and this fact clearly proves that the synthetical hydrocarbon is identical with carvestrene from vestrylamine.

When carvestrene is treated with hydrobromic acid under the conditions mentioned above, only about half of the theoretical quantity of crystalline hydrobromide is obtained. If the porous porcelain, used in its purification, is extracted with ether and the ethereal solution evaporated, a heavy oil is obtained which contains about 50 per cent. of bromine and deposits only a few crystals on long standing. This behaviour seems to point, as Baeyer has suggested, to the formation of *cis-* and *trans*-modifications when carvestrene reacts with hydrobromic acid.

The cis- *and* trans-*Modifications of Tetrahydrocarvestrenediol* (m-*Menthane*-1 : 8-*diol*).



$$CH_2<\begin{matrix}CMe(OH)\cdot CH_2\\ CH_2\text{———}CH_2\end{matrix}>CH\cdot CMe_2\cdot OH.$$

When dihydrocarvestrenol (10 grams) was mechanically shaken with 5 per cent. sulphuric acid (350 c.c.) it gradually dissolved and, after remaining for ten days, the clear solution was saturated with ammonium sulphate and extracted twenty times with pure ether. The ethereal solution was dried over calcium chloride and evaporated, when a thick syrup resulted which soon began to crystallise and ultimately became almost solid. After remaining in contact with porous porcelain until quite free from oil, the residue was rapidly washed with a little ether and recrystallised from this solvent:

0·1408 gave 0·3600 CO_2 and 0·1458 H_2O. $C = 69·7$; $H = 11·5$.

$C_{10}H_{20}O_2$ requires $C = 69·8$; $H = 11·6$ per cent.

cis-*Tetrahydrocarvestrenediol* is readily soluble in dry ether and separates from the concentrated solution as a voluminous mass of slender needles; it melts at about 90°, and is excessively soluble in water.

In order to determine whether this substance combined with water to form a hydrate, corresponding to *cis*-terpin hydrate, it was dissolved in a little water and the solution allowed to evaporate under ordinary conditions. The crystalline residue was left exposed to the air until dry and then analysed:

0·1126 gave 0·2871 CO_2 and 0·1169 H_2O. $C = 69·5$; $H = 11·6$.

$C_{10}H_{20}O_2$ requires $C = 69·8$; $H = 11·6$ per cent.

It is therefore obvious that *cis*-tetrahydrocarvestrenediol does not yield a hydrate under these conditions. *cis*-Tetrahydrocarvestrenediol dissolves in a solution of hydrogen bromide in acetic acid (saturated at 0°) and, on standing, crystals gradually separate. These were collected and recrystallised from methyl alcohol, when colourless needles were obtained which melted at 48—49° and consisted of *trans*-carvestrene dihydrobromide. The acetic acid mother liquor from these crystals gave, on dilution with water, a quantity of an oily bromo-compound which was doubtless the crude *cis*-modification.

trans-*Tetrahydrocarvestrenediol*.—This interesting substance was first prepared, in small quantities, by Baeyer (*Ber.*, 1894, **27**, 3490), and found to melt at 127°, but it was not analysed. We have repeated Baeyer's experiments, using material prepared from synthetical carvestrene, with the following results. *trans*-Carvestrene dihydrobromide (5 grams) was dissolved in glacial acetic acid (50 grams) in the cold, and silver acetate (10 grams) added in small quantities at a time, the whole being shaken after each addition and any rise of temperature avoided by cooling in ice-water. The decomposition took place at once with separation of silver bromide, and, after remaining overnight, the product was filtered and the silver bromide washed with a little acetic acid. The filtrate was then mixed with water, neutralised with potassium carbonate, and repeatedly extracted with ether. The ethereal solution, on evaporation, deposited an oily acetate which was digested with methyl-alcoholic potash (containing 5 grams of KOH) for a few minutes; water was then added and the *trans*-tetrahydrocarvestrenediol repeatedly extracted with ether. After washing with a little water, the ethereal solution was dried over calcium chloride and evaporated, when a crystalline mass remained which melted at 118—122°. This was dissolved in much light petroleum (b. p. 70—75°) and the solution rapidly concentrated, during which operation the pure substance separated in long, slender needles:

0·0854 gave 0·2165 CO_2 and 0·0913 H_2O. C = 69·2; H = 11·8.

$C_{10}H_{20}O_2$ requires C = 69·8; H = 11·6 per cent.

trans-*Tetrahydrocarvestrenediol* melts at 126—127°, and is very readily soluble in water, alcohol, or ether, but very sparingly so in cold light petroleum.

Direct Synthesis of Dihydrocarvestrenol [Δ^1-m-*Menthenol* (8)], *Tetrahydrocarvestrenediol* (m-*Menthane*-1 : 8-*diol*), *and its Anhydride* (m-*Cineol*) *from Ethyl* cyclo*Hexanone-3-carboxylate.*

In describing the preparation of 1-methyl*cyclo*hexanol-3-carboxylic acid from ethyl *cyclo*hexanone-3-carboxylate and magnesium methyl iodide, attention was called to the fact that a neutral oil (B, p. 495) with a strong odour of camphor is formed in considerable quantity during the reaction. This oil was collected from several experiments, and when 75 grams had accumulated it was fractionated under reduced pressure (20 mm.), when about 30 grams distilled at 85—95°, 25 grams at 95—120°, and most of the remainder (10 grams) at 130—150°.

The fraction 85—95° (20 mm.) was again distilled under the same pressure, when 23 grams passed over below 85°, and on fractionating this under ordinary pressures, and finally over sodium, an oil was obtained which distilled constantly at 177—178°, and consisted of the nearly pure *anhydride* of cis-*tetrahydrocarvestrenediol* (m-*cineol*):

0·1482 gave 0·4258 CO_2 and 0·1583 H_2O. C = 78·4; H = 11·9.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

The oil was, however, unstable to permanganate, and evidently contained traces of some unsaturated substance, probably carvestrene; it was therefore shaken with ice and very dilute permanganate and again fractionated, when the analytical results were more satisfactory:

0·1186 gave 0·3388 CO_2 and 0·1268 H_2O. C = 78·1; H = 11·8.

m-*Cineol* is a colourless oil readily volatile in steam, which possesses a most pungent odour of camphor and distils at 177—178° (765 mm.).

It appears to form salts similar to those which are so characteristic of ordinary cineol, but the amount of material available was not sufficient to allow of these being investigated.

Unlike carvestrene, *m*-cineol dissolves at once in a saturated solution of hydrobromic acid in acetic acid with evolution of heat, and in a few minutes the solution clouds and an oil separates, but even after remaining for several days in a cool place this did not show any signs of crystallising. The product was diluted with water, extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride and evaporated, and the residue exposed over sulphuric acid in an evacuated desiccator.

A very small quantity of *trans*-carvestrene dihydrobromide (m. p. 48—49°) slowly separated, and the oil was found to contain 49·4 per cent. of bromine. There can therefore be little doubt that the main product of the action of hydrobromic acid at low temperatures on *m*-cineol is *cis*-carvestrene dihydrobromide.

The second fraction of the neutral oil boiling at 95—129° (20 mm.) was repeatedly fractionated, and yielded a large quantity of an oil which distilled constantly at 105—108° (30 mm.), and was found to be *dihydrocarvestrenol*:

0·1092 gave 0·3113 CO_2 and 0·1152 H_2O. C = 77·6; H = 11·7.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

The highest fraction, 130—150° (20 mm.), gradually deposited crystals, and after some weeks the semi-solid mass was left in contact with porous porcelain until the oily impurity had been absorbed, and the colourless residue was then crystallised from light petroleum, from which long, slender needles separated. This substance melted at

126—127°, and was found to be trans-*tetrahydrocarvestrenediol*, since, when mixed with the specimen of this substance obtained as explained on p. 502, no alteration in the melting point could be observed.

The authors are greatly indebted to the Research Fund Committees both of the Royal Society and of the Chemical Society for grants which have largely defrayed the heavy cost of this investigation.

The Victoria University,
Manchester.

L.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part IX. A New General Method for Studying Intramolecular Change.*

By Thomas Stewart Patterson and Andrew McMillan, M.A.

It has been shown in previous parts of this investigation (Trans., 1905, **87**, 313) that the rotation of ethyl tartrate may be considerably modified by admixture with inactive substances, and it is particularly noticeable that, in many cases, comparatively large effects are produced by small quantities of the inactive constituents. Thus, for instance, whilst the rotation of pure ethyl tartrate is +9·354°, the addition of 25 per cent. of water raises it to +10·242°, and the addition of 20 per cent. of chloroform lowers it to +5·528°.

A consideration of the changes of rotation produced, either in concentrated or dilute solution by the addition of inactive solvents, suggested a further line of research, namely, an examination of the relative effects of isomeric solvents in modifying the rotation of active compounds, a problem which is at present being investigated. That symmetrical ethyl sulphite and asymmetrical ethyl sulphite, to take an example, will produce different effects on the rotation of an active compound dissolved in them is practically certain, but as to the magnitude of the difference, we can at present say nothing. This idea, however, in turn suggests the further possibility that if a substance capable of undergoing intramolecular change be dissolved in, say, ethyl tartrate, the rearrangement of the molecule of the former might be indicated and followed by the gradual alteration in the rotation of the latter, since the two different modifications of the inactive substance might have different solvent influences.

The present paper gives an account of some experiments which we have instituted in this direction. We chose as the first subjects for examination the two oximes of benzaldehyde, passing then to anisaldoxime and to ethyl formylphenylacetate. In each case our expectations were realised, the results, especially in the case of the oximes, being of a much more striking character than could have been anticipated.

The polarimeter has, of course, often been used to follow the course of a chemical reaction as, for instance, the inversion of sucrose, which was studied by Wilhemy, or the mutual conversion of the nitro- and ψ-nitro-derivatives of camphor and π-bromo-camphor which Lowry (Trans., 1899, **75**, 211) has described, but in all such cases the substance which undergoes change is the active compound itself, a condition which greatly limits the applicability of the method.

A polarimetric method which would make it possible to follow molecular change in inactive substances would obviously be of great service in various directions, and the possibility of establishing such a method, and one too of a general character, is certainly indicated by the above considerations.

EXPERIMENTAL.

It was of interest, to begin with, to ascertain the influence of benz*anti*aldoxime on the rotation of ethyl tartrate, so we first directed our attention to this point.

The benz*anti*aldoxime was prepared in the usual manner. It boiled at 122—123° at 19 mm. (oil-bath, 160°).

Determination of its density gave the following results:

Temperatures ...	18°	22°	26°	38°
Densities	1·11232	1·10854	1·10573	1·0957

*Rotation of Ethyl Tartrate in Benz*anti*aldoxime.*

*p : 79·90.

$t°$.	$\alpha_D^{t°}$ (40 mm.).	Density.	$[\alpha]_D^{t°}$.
16·4	+4·90°	1·1932	+12·85°
41·2	5·15	1·1680	13·79
61·3	5·32	1·1474	14·52
79·5	5·60	1·1285	15·52
94·4	5·80	1·1130	16·26
15·9	4·85	1·1938	12·71

Densities determined:

Temperatures	44·6°	47·5°	54·8°	64·75°	74·0°
Densities	1·1647	1·1616	1·1539	1·1443	1·1348

* p = grams of ethyl tartrate per 100 grams of solution.

p: 49·6228.

$t°$.	$\alpha_D^{t°}$ (70 mm.).	Density.	$[\alpha]_D^{t°}$.
13·8°	+4·25°	1·1644	+10·51°
20·5	4·40	1·1582	10·94
30·0	4·62	1·1493	11·57
37·8	4·80	1·1420	12·10
47·8	5·04	1·1326	12·81
67·1	5·45	1·1144	14·12
84·6	5·81	1·0980	15·23
91·1	5·94	1·0915	15·63
114·1	6·15	1·0720	16·53
131·5	6·30	1·0548	17·19
14·3	4·40	1·1640	10·88

Densities determined:

Temperatures	18°	22°	28·75°	40°
Densities	1·1605	1·1565	1·1504	1·1399

p: 22·819.

$t°$.	$\alpha_D^{t°}$ (70 mm.).	Density.	$[\alpha]_D^{t°}$.
17·5	−0·04°	1·1352	−0·22°
26·1	+0·24	1·1274	+1·33
38·0	+0·60	1·1168	+3·36
41·2	+0·70	1·1140	+3·93
16·0	−0·08	1·1365	−0·37
56·4	+1·16	1·1101	+6·58
68·1	+1·52	1·0905	+8·73
82·3	+1·90	1·0780	+10·80
96·0	+2·12	1·0660	+12·45
117·5	+2·46	1·0484	+14·69

Densities determined:

Temperatures...	22°	28°	34·5°	45°	54·75°	77·7°
Densities.........	1·1313	1·1261	1·1204	1·1112	1·1027	1·0823

p: 10·372.

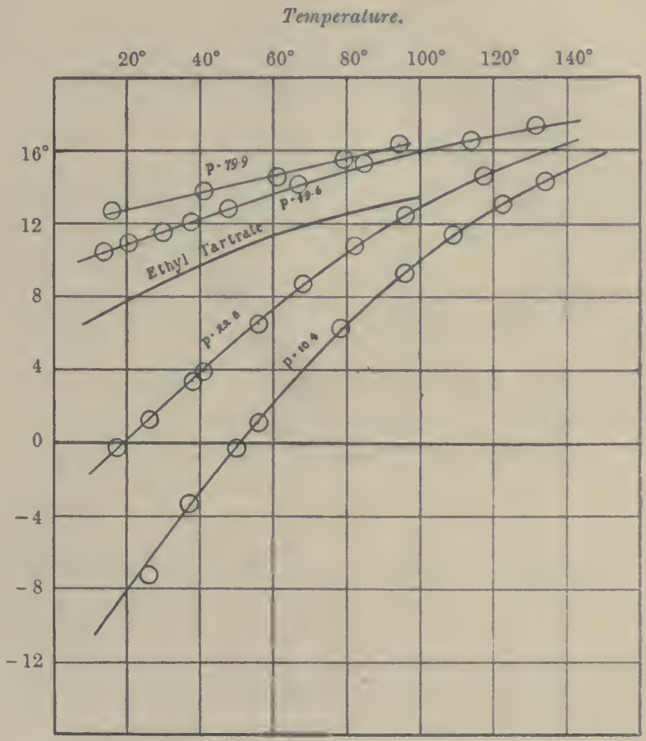
$t°$.	$\alpha_D^{t°}$ (100 mm.).	Density.	$[\alpha]_D^{t°}$.
26·0°	−0·84°	1·1160	−7·26°
37·0	−0·39	1·1065	−3·38
56·1	+0·12	1·0905	+1·07
78·5	+0·70	1·0710	+6·30
96·0	+1·02	1·0565	+9·31
109·0	+1·24	1·0456	+11·43
122·5	+1·41	1·0392	+13·08
134·0	+1·52	1·0245	+14·30

Densities determined:

Temperatures	21·5°	27·5°	33·6°	40·5°	44·5°
Densities	1·11976	1·11483	1·1096	1·1037	1·1003

The curves, which may be obtained from these data, showing the relationship between specific rotation and temperature, are reproduced in Fig. 1, the graph for homogeneous ethyl tartrate being also shown for comparison. It will be observed at once that benz*anti*aldoxime has a very remarkable effect on the rotation of ethyl tartrate. Whereas the rotation-temperature curves for the $p:80$ and $p:50$ solutions lie above that for the pure ester, those for solutions of $p:23$ and $p:10$ lie below it, at least at temperatures less than 100°. A behaviour similar to this has been observed in other cases, but the remarkable effect which dilution produces on the rotation of the dissolved ethyl tartrate is much more striking than in any other case hitherto examined. A $p:10$ solution which has $[\alpha]_D$ $-7{\cdot}7°$ at 20°, 15·4° less than the pure ester, is inactive at about 51°, and at 100° has $[\alpha]_D$ $+10°$ which is only 3·5° less than that of the pure ester. The cause, therefore, which brings about the diminution of rotation is very rapidly overcome by rise of temperature.

FIG. 1.

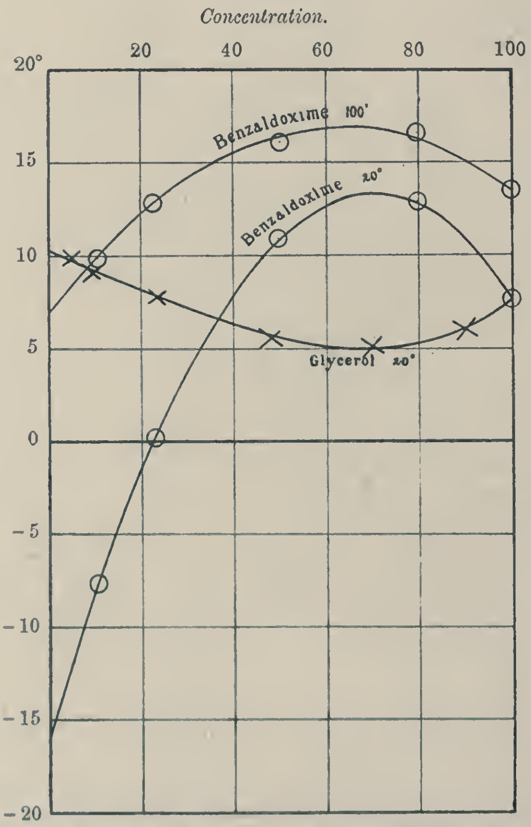


Temperature-rotation curves. Ethyl tartrate in benzantialdoxime.

By interpolation from these curves we find for the specific rotations of the solutions at 20° and 100° the following numbers:

p.	$[\alpha]_D^{20°}$.	$[\alpha]_D^{100°}$.	p.	$[\alpha]_D^{20°}$.	$[\alpha]_D^{100°}$.
100·0	+7·76°	+13·5°	22·82	+0·2°	+12·8°
79·9	+12·9	+16·4	10·37	−7·7	+9·9
49·62	+10·8	+16·1	0·0	−16·0	+7·0

FIG. 2.



Concentration-rotation curves. Ethyl tartrate in benzantialdoxime and in glycerol.

From these data, the complete curves (benz*anti*aldoxime) in Fig 2 have been drawn. The rotation of the pure ester is +7·76° at 20°. Addition of oxime increases this rotation gradually until $p:70$, when a maximum value for the specific rotation of +13·6° is reached. Further addition of oxime then diminishes the rotation, which has in a solution of $p:37$ the same value as the homogenous ester; a solution of $p:22$ is inactive, whilst a $p:10$ solution has a rotation equal in magnitude, but opposite in sign to that of the pure ester. At infinite dilution the specific rotation would be approximately −16°. The rotation therefore varies some 30° between the extreme limits and by about equal amounts on either side of zero.

The concentration-rotation curve at 100° is also shown in the diagram. It is obviously of the same kind as the curve for 20°, but somewhat modified in form. The maximum occurs in both at almost the same concentration, $p:70$, and it is worthy of note that the concentration corresponding to a mixture of 1 molecule ethyl tartrate and 1 molecule oxime is $p:63$.

In this, then, as in other cases, the influence of changing concentration on rotation is much less striking at 100° than at 20°, although in the present instance still very remarkable.

The solvent which causes a variation most like this is glycerol (Trans., 1901, 79, 178). The concentration curve for ethyl tartrate in glycerol at 20° is shown in Fig. 2 for comparison. It will be observed that it is similar in character to that for the oxime, but in an exactly opposite sense. Addition of glycerol to ethyl tartrate gradually depresses the rotation of the ester to reach a minimum value at $p:68$ at 20°. Further addition of glycerol increases the rotation to reach +7·76° at $p:26$, whilst the value at infinite dilution is +10·6°.

The peculiar form of the concentration-rotation curve for the oxime might perhaps encourage the idea that at $p:70$ the oxime exists chiefly in one form, whilst in dilute solution the other form preponderates, but our subsequent experiments seem to show that this is not the case, and that the remarkable form of this curve must be otherwise explained.

Experiments with Benzsynaldoxime.—Having thus established the influence of benz*anti*aldoxime on the rotation of ethyl tartrate. we proceeded to a study of the behaviour of mixtures of ethyl tartrate with benz*syn*aldoxime.

Benz*syn*aldoxime was prepared from its hydrochloride by the action of slightly more than the calculated quantity of sodium carbonate solution. The solid after washing and thorough drying was crystallised as rapidly as possible from dry chloroform heated to about 50°. The preparation used melted at 127°.

We first made up a solution of $p:90·11$ (that is, one containing 9·89 per cent. of *syn*oxime). The oxime did not dissolve very readily and slight heating was necessary. This solution was examined in a 100 mm. tube in the polarimeter. At 17·3° the observed rotation was +11·38°, and after standing for half an hour this had fallen to 11·18°. The rotation was thus changing gradually, and to accelerate the alteration the tube containing the solution was heated to 50° for more than an hour and allowed to cool.

On the following morning the rotation had become +8·15° at 17·3°. No further alteration was observed.

Now it is well known that benz*syn*aldoxime readily changes into benz*anti*aldoxime, and it was necessary to ascertain whether the above solution, after a constant rotation had been reached, corresponded with the solutions of *anti*oxime which had been examined previously. Its rotation was therefore redetermined, after constant rotation had been reached, at several temperatures, with the following results:

p : 90·11.

$t°$.	$\alpha_D^{t°}$ (100 mm.).	Density.	$[\alpha]_D^{t°}$.
17·3°	+8·15°	1·2012	+10·76°
27·8	8·52	1·1903	11·35
44·0	9·15	1·1740	12·36
20·0 *	8·25 *	1·1982	10·85 *

Densities determined:

Temperatures	21·1°	26°	34·25°	43·50°
Densities	1·1975	1·1922	1·1835	1·1746

* Interpolated.

The value $[\alpha]_D^{20°}$ +10·85, for this solution thus falls exactly on the concentration curve deduced from solutions of the *anti*oxime, and therefore the *syn*oxime had been converted completely into the *anti*-form. The solution behaved exactly as if it had been made up originally with the *anti*-form although its behaviour at first was totally different. The magnitude of the change in the rotation of the ethyl tartrate due to this intramolecular rearrangement is most striking. Mixture with *anti*oxime, as has been shown, raises the rotation of the ethyl tartrate, but mixture with the *syn*oxime has a much more pronounced effect in the same direction. The observed rotation in this instance fell from +11·38° to +8·15°, or by 3·23° for only 100 mm., and it must be remembered that +11·38° is not the true initial value for the solution of the *syn*oxime, since the rotation had been falling during the preparation of the mixture, and whilst it was lying in the jacket of the polarimeter to attain uniform temperature.

That this very considerable change could be brought about by rearrangement of only 9·89 per cent. of inactive substance indicated a very simple means whereby the velocity of transformation of *syn*-aldoximes into *anti*aldoximes under varying external conditions could be measured directly and easily in ethyl tartrate solution, an optical method being of course by far the best for the purpose since the substance undergoing change may be left entirely undisturbed during the course of the reaction.

Certain reactions of the oximes have already been submitted to measurement. Thus Hantzsch (*Zeitsch. physikal. Chem.*, 1894, 13, 509) has determined the velocity with which the acetates of the *syn*oximes are converted into nitriles in aqueous ethyl-alcoholic solution, whilst Ley (*Zeitsch. physikal. Chem.*, 1895, 18, 376) has studied the influence of temperature on the velocity of this reaction and has also, by an ingenious but somewhat difficult method, measured the velocity of transformation of the acetates of the *syn*oximes into the corresponding salts of the *anti*oximes under the influence of hydrochloric acid, but no method has hitherto been available for measuring the rate of transformation of a *syn*- into an *anti*-oxime.

We therefore proceeded to test our method, using a solution containing less oxime, the results being given in the following table. The values for initial rotation are obtained by extrapolation, and the time in minutes after preparation of the solution is given in the column headed T:

$p : 92·82$. $a = 4·37°$. Temperature 20°.

T (minutes).	$a_D^{20°}$ (100 mm.).	$a - x$.	$1000\ k$.
0	+15·60°	—	—
45	15·1	3·87°	2·69
80	14·8	3·57	2·53
130	14·53	3·30	2·16
155	14·45	3·22	1·96
1115	12·625	1·395	1·09
3975	11·23	—	—

Now the transformation of a *syn*- into an *anti*-oxime ought to be a unimolecular reaction, and if we assume that the change of rotation of the ethyl tartrate is directly proportional to the change of concentration of the *syn*oxime we obtain the second and third columns in the above table, where a^0 = total change of rotation, x^0 is proportional to quantity of *syn*oxime transformed after time T, and k is calculated from equation:

$$k = \frac{1}{T} \log_e \frac{a}{a - x}.$$

The values thus obtained for k are not constant. The velocity of the transformation seems to be nearly 3 initially, diminishing, however, to about one-third of this value after 1000 minutes. The time required for one quarter of the transformation to take place is roughly 140 minutes, for half-change 490 minutes, and for three-quarter change 1190 minutes.

It was found in preparing the above mixture that the proportion of *syn*oxime used was still rather large to be brought into solution quite easily and, therefore, the next solution examined contained less oxime. The data for this solution were found as follows:

$p:95{\cdot}2$. Temperature 20°. $a=3{\cdot}25°$.

T (minutes).	α^2 (100 mm.).	$a-x$.	1000 k.
0	13·95°	—	—
25	13·76	3·06°	2·41
40	13·60	2·90	2·85
85	13·33	2·63	2·49
130	13·13	2·43	2·23
220	13·00	2·30	1·57
295	12 83	2·13	1·43
360	12·73	2·03	1·31
415	12·60	1·90	1·29
1355	11·43	0·73	1·20
1590	11·25	0 55	1·12
1830	11·13	0·43	1·10
2840	10·73	—	—
3150	10·70	—	—
4170	10·70	—	—

It will be observed that the behaviour here is much the same as in the previous instance. The velocity of transformation falls off gradually as time elapses. It is possible that the value of k after 25 minutes is incorrect. From about 80 minutes on the values are almost the same as in the $p:92{\cdot}82$ solution, and the initial value is also probably nearly 3.

Influence of Temperature on the Velocity of Transformation.

We next proceeded to determine the influence of temperature on the velocity of transformation of the oxime, using two solutions of as nearly as possible $p:95$. The results are recorded below. The temperature ($t°$) was kept as near 32·4° and 42·9° as we could, but it varied slightly :

$p:95{\cdot}10$. $a=2{\cdot}56°$.

T (minutes).	$t°$.	α_D^t (100 mm.).	$a-x$.	1000 k.
0	—	+14·3°	—	—
15	32·4°	14·14	2·4°	4·27
45	32·4	13·84	2·10	4·40
80	32·8	13·60	1·86	3·99
120	32·4	13·33	1·59	3·97
175	32·4	13·07	1·33	3·74
245	32·5	12·76	1·02	3·75
360	32·5	12·42	0·68	3·68
390	32·5	12·30	0·56	3·89
450	33·1	12·20	0·46	3·81
1190	32·8	11·74	—	—
1260	33·0	11·74	—	—

$p : 95{\cdot}2. \quad a = 2{\cdot}5^\circ.$

T (minutes).	t°.	a^{t°.	$a - x$.	1000 k.
0	—	+15·00	—	—
15	42·9°	14·62	2·12°	11·0
30	42·9	14·28	1·78	11·3
75	42·8	13·61	1·11	10·8
160	42·8	12·97	0·47	10·4
225	42·5	12·74	0·24	10·4
310	42·8	12·58	0·08	11·1
360	42·8	12·53	0·03	12·3
510	42·6	12·50	—	—
590	42·5	12·50	—	—

The initial velocities for these solutions found by plotting curves are about 4·6 and 11 respectively.

In regard to the data for these two solutions, two facts may be noticed. In the first place, the velocity of transformation increases rapidly with rise of temperature, having at 20° an initial value of about 3, at 32·4° one of about 4·6, and at 42·9° one of 11. In the second place it is very noticeable that whilst at 20° the values found for k diminish as time elapses, the diminution in the value of k at 32·4° is distinctly less, and at 42·9° k is practically a constant.

The variation in the value of k at the lower temperatures is perplexing. It may possibly be due to some tendency of the *syn*oxime and tartrate to combine with each other, the combination taking place only slowly. This might hinder the change of the *syn*- into the *anti*-form, and diminish the rate of transformation, but it does not seem to prevent the change, since the solutions made up with *syn*oxime assume, ultimately, exactly the same rotation values as solutions made up with the *anti*oxime.

It seemed of interest .to ascertain if there exists in solution any equilibrium between *syn*- and *anti*-form. We therefore prepared solutions of ethyl tartrate and solid benz*anti*aldoxime, m. p. 35° (which dissolves very readily), but we were unable with the means at our disposal to detect any increase in the rotation of these on standing; the change appears to be irreversible.

Another explanation of the inconstancy of k at 20° occurred to us. In making our calculation we have assumed that the change in rotation is directly proportional to the amount of *syn*oxime transformed, but it is possible that this might not be so. To test the point, we made up several solutions, each containing the same total amount of oxime, but made up by mixing the *syn*- and *anti*-oximes in varying proportions.

These experiments were carried out with a fresh preparation of ethyl tartrate which, unfortunately, does not seem to have been quite pure.

It had been twice distilled, and gave $\alpha_D^{19·3°}+9·45$,* but it possibly contained some moisture. The results are therefore not strictly comparable with the preceding, but they serve to elucidate the point under consideration :

I.—Ethyl tartrate......95·09 }
*syn*Oxime........... 4·91 }. Temperature 20°. $a=2·7°$

T (minutes).	$\alpha_D^{20°}$ (100 mm.).	$a-x$.	1000 k.
0	+13·20°	—	—
25	12·72	2·22°	7·83
65	12·32	1·82	6·06
150	11·92	1·42	4·28
220	11·66	1·16	3·83
1235	10·66	0·16	2·28
1370	10·50	—	—
∞	10·50	—	—

II.—Ethyl tartrate.........95 per cent.
Benz*syn*aldoxime...... 4 ,,
Benz*anti*aldoxime ... 1 ,,
$a=2·19°$.

T (minutes).	$\alpha_D^{20°}$ (100 mm.).	$a-x$.	1000 k.
0	+12·70°	—	—
35	12·36	1·85°	5·11
105	11·96	1·45	3·89
165	11·81	1·30	3·16
225	11·70	1·19	2·71
540	10·70	0·19	1·93
2600	10·51	—	—

III.—Ethyl tartrate............95·06 per cent.
Benz*syn*aldoxime ...... 2·47 ,, }
Benz*anti*aldoxime ...... 2·47 ,, } 4·94.
$a=1·2°$.

T (minutes).	$\alpha_D^{20°}$ (100 mm.).	$a-x$.	1000 k.
0	+11·70°	—	—
50	11·46	0·96°	4·46
115	11·30	0·80	3·52
220	11·16	0·66	2·71
320	11·03	0·53	2·55
1395	10·68	0·18	1·36
1525	10·65	0·15	1·36
1660	10·61	0·11	1·43
2800	10·50	—	—

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* This is very near the rotation of pure ethyl tartrate, but since water raises the rotation of ethyl tartrate, the presence of a small quantity of moisture may easily escape detection.

IV.—Ethyl tartrate............95·10 per cent.
Benz*syn*aldoxime ...... 0·98 ,, } 4·90
Benz*anti*aldoxime ...... 3·92 ,, }
$a = 0·54°$.

T (minutes).	$a_D^{20°}$ (100 mm.).	$a - x$.	1000 k.
0	+11·04°	—	—
35	10·90	0·40°	8·57
65	10·80	0·30	9·04
140	10·73	0·23	6·09
1280	10·50	—	—

V.—Ethyl tartrate.........95·02 per cent.
Benz*anti*aldoxime ... 4·98 ,,
$a_D^{20°} + 10·50$.

The values for the initial rotations of these solutions were obtained by graphic extrapolation. When they in turn are plotted relative to concentration they are found to lie practically on a straight line, so that our assumption that the change in rotation is proportional to the concentration of the *syn*oxime is justified.

The first of these solutions ought to have corresponded exactly with that for which data are given on p. 512, but this is not the case. Both the initial and end rotations are different, and k is considerably higher. This, as has been remarked, was due to insufficient purification of this sample of ethyl tartrate.

The values of k ought to be the same for all the solutions, and that this is not the case is, we think, due chiefly to the fact that these mixtures were made by heating the constituents together in a small open flask in a warm-water bath, and that possibly traces of moisture may have been introduced in this way in the first and last. The first three solutions agree fairly well, and it must be remembered that in the last the total change was small.

Experiments with Anisaldoxime.—It seemed next of interest to ascertain whether the behaviour we have observed with the benzaldoximes was a specific property of these substances or whether it applied to oximes generally. We used for the purpose some anis*syn*aldoxime prepared by Mr. Andrew Henderson, M.A., B.Sc., to whom we have pleasure in expressing our thanks. The *syn*oxime used was recrystallised in small quantities from warm benzene. It melted at 125°.

Anis-syn*aldoxime in Ethyl Tartrate.*

$p:95·13$. *Temperature* 20°. $a = 2·504°$.

T (minutes).	$\alpha_D^{20°}$ (100 mm.).	$a - x$.	1000 k.
0	+13·77°	—	—
25	13·533	2·267°	3·95
50	13·343	2·077	3·72
165	12·563	1·297	3·98
210	12·383	1·117	3·84
285	12·088	0·822	3·91
370	11·863	0·597	3·87
430	11·749	0·483	3·83
605	11·499	0·233	3·92
∞	11·266	—	—

A solution of concentration similar to the preceding one, but made up with anis*anti*aldoxime, gave a rotation at 20° which agrees with the end rotation of the *syn*oxime solution.

If we compare the values of k found for this solution with those already given for a $p:95$ solution of benzaldoxime, we find that, while the velocity of change is somewhat higher and the total change of rotation less, the constancy of k is much better. Quarter change takes place in about seventy-five minutes, half change in 175 minutes, and three-quarter change in 360 minutes.

We next examined anis*syn*aldoxime in a mixed solution of ethyl tartrate and *iso*butyl alcohol, and also in a solution of ethyl tartrate and benzene, with the object of ascertaining the relative influences of *iso*butyl alcohol and benzene on the velocity of the intramolecular change.

The results are given below :

Anis-syn*aldoxime, Ethyl Tartrate and* iso*Butyl Alcohol.*

Composition of solution:
*iso*Butyl alcohol = 73·17 per cent.
Ethyl tartrate = 24·39 ,, ,,
Anis-*syn*aldoxime = 2·44 ,, ,, } $p:9·10$ of oxime.

$$\text{Ratio}\ldots\ldots\ldots\ldots \frac{E.T.}{\text{Oxime}} = \frac{10}{1}.$$

Temperature 20°. $a = 0·368°$.

T (minutes).	$\alpha_D^{20°}$ (400 mm.).	$a - x$.	1000 k.
0	+6·778°	—	—
45	6·726	0·316°	3·37
95	6·686	0·276	3·02
210	6·617	0·207	2·73
345	6·534	0·124	3·15
2805	6·410	—	—
∞	6·410	—	—

Anis-syn*aldoxime Ethyl Tartrate and Benzene.*

Composition of solution:
Benzene = 73·29 per cent.
Ethyl tartrate = 24·27 „ „
Anis-*syn*aldoxime = 2·44 „ „ } p : 9·135 of oxime.

Ratio............ $\frac{E.T.}{\text{Oxime}} = \frac{10{\cdot}05}{1}$.

Temperature 20°. $a = 3{\cdot}667°$.

T (minutes).	$a^{20°}_{D}$ (400 mm.).	$a - x$.	1000 k.
0	8·980°	—	—
50	7·713	2·400°	8·48
105	6·794	1·481	8·63
150	6·289	0·976	8·82
200	5·988	0·675	8·46
235	5·863	0·550	8·07
270	5·713	0·400	8·21
1310	5·313	—	—

From these data it appears that the change in rotation in the solution containing *iso*butyl alcohol is comparatively slight. The values for k, however, agree fairly closely and do not seem to diminish with lapse of time.

The numbers for the benzene solution are most striking. The total change in rotation is considerable, 3·667°, the velocity of change is much greater than in *iso*butyl alcohol or in undiluted ethyl tartrate and the values for k show a very fair constancy.

We also examined a solution similiar to the last two, but containing chloroform as a third constituent. The result was as follows:

Anis-syn*aldoxime, Ethyl Tartrate and Chloroform.*

Composition of solution:
Chloroform = 73·24 per cent.
Ethyl tartrate = 24·31 „ „
Anis-*syn*aldoxime = 2·45 „ „ } p : 9·16 of oxime.

Ratio............ $\frac{T.}{\text{Oxime}} = \frac{9{\cdot}92}{1}$.

Temperature 20°. $a = 0{\cdot}15$.

T (minutes).	a^{20}_{D} (400 mm.).	$a - x$.	1000 k.
0	−1·600°	—	—
115	1·544	0·094°	4·06
180	1·514	0·064	4·73
265	1·450	—	—
1300	1·450	—	—

The alteration in rotation is very small, and this is probably due to the great depressing influence of chloroform on the rotation. Chloroform has so great an influence in this direction that it might be expected that a small proportion of another substance, even if exceptionally powerful, would only have a very slight effect. It is particularly noticeable that whereas in all cases examined, the rotation is raised by addition of *syn*oxime and gradually falls, in chloroform the depressed rotation is raised by addition of *syn*oxime and that change into *anti*-oxime brings about a further rise in rotation. On account of the change of rotation being so small we lay no stress on the values of the constant which can be calculated from the rotation data, although we have included the numbers in the table.

Experiments with Ethyl formylphenylacetate.—In order to ascertain if this method was applicable also to other types of intramolecular change, we obtained some of each of the two forms of formylphenylacetic ethyl ester * and examined solutions of these in ethyl tartrate. In mixtures containing 5 per cent. of the acetic ester the change in rotation was very slight. We therefore prepared a $p:60{\cdot}44$ solution of the solid (β or aldo) form in ethyl tartrate. Heating was necessary to bring about solution and on cooling to 20° the solid ester crystallised out. We, therefore, determined the rotation of this mixture at several higher temperatures in order to obtain the value for 20° by extrapolation.

The following are the data :

t°.	$\alpha_{D}^{t^\circ}$.	t°.	$\alpha_{D}^{t^\circ}$.	t°.	$\alpha_{D}^{t^\circ}$.
58·6°	+4·77°	43·5°	+4·69°	29·0°	+4·58°

The value at 20° by extrapolation is +4·53°, but we found that after the heating necessary in these experiments the acetic ester no longer crystallised out on cooling and the rotation could be determined even at 11·5° when its value was +4·44° which is in agreement with the numbers given above. Since the acetic ester did not crystallise out, it is apparent that change had taken place and this may have been accompanied by some alteration in rotation, but this was probably slight since the value found at 11·5° after the mixture had stood overnight agreed with those obtained at higher temperatures.

We then prepared a similar solution of the liquid (α or enol) form, which is the less stable, and were able to observe in this case a distinct, although not very great, change at 20°. The results were as follows :

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* Our thanks are due to Mr. R. Boyd who prepared these for us.

Ethyl Formylphenylacetate (*a-form*) *in Ethyl Tartrate* $p:59\cdot90$.

Temperature 20°. $a = 0\cdot424°$.

T (minutes).	$a_D^{20°}$ (50 mm.).	$a-x$.	1000 k.
0	+3·972°	—	—
65	4·066	0·330°	3·84
190	4·149	0·247	2·78
310	4·199	0·197	2·47
1390	4·316	0·080	1·19
1540	4·349	0·047	1·42
∞	4·396	—	—

In this case the rotation of the solution increases gradually and by nearly one degree for a length of 100 mm. The constant obtained from our data is not very satisfactory, diminishing to a considerable extent with lapse of time. Possibly the cause may be the same as that which operates in the case of benz*syn*aldoxime in ethyl tartrate. The results are promising, however, and indicate that we have in this method a means of following quantitatively changes that have hitherto only been susceptible of qualitative examination. The method, we think, may be fairly described as general, inasmuch as, although it may fail in certain cases, it is probable that some active compound may always be found the rotation of which will alter in response to intramolecular change in an inactive substance.

The experiments which we have recorded here are to some extent of a preliminary character. The apparatus which we have used was not specially designed for the purpose and we intend with more suitable and more delicate appliances to extend this investigation in some of the many directions that readily suggest themselves—to the influence of various media on velocity of transformation, to the use of other active substances as media, and to the investigation of various examples of tautomeric change.

THE UNIVERSITY,
GLASGOW.

LI.—*Camphor-β-sulphinic Acid and Camphorylsulphonium Bases.*

By SAMUEL SMILES and THOMAS P. HILDITCH.

IN a previous communication to the Society one of the present authors and Le Rossignol showed (Trans., 1906, **89**, 696) that aromatic sulphinic acids may be converted to salts of sulphonium bases by condensation with phenolic ethers in accordance with the following equation:

$$\mathrm{Ar{\cdot}SO_2H + 2Ar{\cdot}OEt = Ar(Ar{\cdot}OEt)_2S{\cdot}OH + H_2O.}$$

The following experiments have been carried out with the object of testing whether this reaction is shown by sulphinic acids other than those of the aromatic series. On account of the rather indefinite character of the purely fatty sulphinic acids we have employed the hydroaromatic camphorylsulphinic acid, which may easily be prepared by the reduction of camphorsulphonic chloride.

The reduction of the chloride of Reychler's camphorsulphonic acid has already been studied by Lowry and Donnington (Trans., 1903, **83**, 479), who employed tin or zinc in acid aqueous media, and thus obtained the corresponding mercaptan. We have found, however, that if zinc dust in alcoholic suspension is employed, a good yield of the zinc salt of camphorylsulphinic acid is obtained. The essential conditions to be observed in this reaction are the dryness of the material and the purity of the zinc dust employed, otherwise the yield of the zinc sulphinate is small. The zinc salt of camphorsulphinic acid is distinguished by the great difference in solubility which it possesses in cold and in hot water; it dissolves with great ease in the cold medium, and if such solutions are heated the salt separates almost completely in the anhydrous state.

The method we have employed for the condensation of camphorsulphinic acid with phenolic ethers is identical with that already described (*loc. cit.*) in the case of aromatic sulphinic acids; it is advantageous, however, to use the zinc salt in place of the free acid, which is somewhat difficult to obtain in a state of purity. When anisole or phenetole is added to a cold solution of zinc camphor-β-sulphinate in concentrated sulphuric acid the liquid assumes a blue colour owing to the formation of the sulphoxide. We have not isolated these sulphoxides but have converted them into the sulphonium bases by adding excess of phenolic ether to the blue solutions mentioned above. The sulphates of the sulphonium bases which are formed in these reactions have not been obtained crystalline; for identification and analysis they were converted into platinichlorides and dichromates. In the following table a comparison is given between the rotatory power of the sulphinic acid and that of the sulphonic acid from which it was prepared:

Molecular Rotations in Aqueous Solution.

	Acid.	Sodium salt.	Zinc salt.
Camphor-β-sulphonic acid	+48	+45·7	+71
Camphor-β-sulphinic acid	−157	−138	−336

It seemed remarkable that such a large change in rotatory power should be caused merely by the change of the sulphonic to the sulphinic group. With the object of ascertaining whether the camphor complex remains unaltered on passing from the sulphonic to the sulphinic acid, we have examined the behaviour of the latter on oxidation. Acidified aqueous solutions of the zinc salt of camphor-β-sulphinic acid are readily oxidised by cold dilute aqueous permanganate. The course of the reaction can be followed by titration in the usual manner, and it was found that one molecule of the zinc salt requires almost the amount theoretically required for the oxidation of the sulphinic acid to the sulphonic acid. Further investigation showed, however, that only about 80—90 per cent. of the sulphinic acid is oxidised to the original camphorsulphonic acid, whilst the remaining 10—20 per cent. is converted into an insoluble substance. From its analysis, molecular weight, and other properties, this substance is evidently the α-disulphone, $C_{10}H_{15}O \cdot SO_2 \cdot SO_2 \cdot C_{10}H_{15}O$, which is produced by the simultaneous oxidation of 2 molecules of the sulphonic acid, thus:

$$2C_{10}H_{15}O \cdot SO_2H + O = C_{20}H_{30}O_6S_2 + H_2O.$$

It is attacked slowly by cold aqueous solutions of alkali hydroxide, but more rapidly by the hot reagent, yielding a mixture of the alkali salts of camphor-β-sulphonic and -sulphinic acids, thus:

$$C_{20}H_{30}O_6S_2 + H_2O = C_{10}H_{15} \cdot O \cdot SO_3H + C_{10}H_{15}O \cdot SO_2H.$$

Kohler and Macdonald (*J. Amer. Chem. Soc.*, 1900, **22**, 224) have already obtained the aromatic α-disulphones by the action of sulphonic chlorides on the sodium salts of aromatic sulphonic acids.

The interaction of aqueous ammonia and camphor-α-disulphone yields the anhydramide of camphor-β-sulphonic acid, prepared by Armstrong and Lowry from the chloride of that acid (Trans., 1902, **81**, 1448). Experiments have also been made in the oxidation of the sulphinic acid in alkaline solution, and the results have shown that camphor-β-sulphonic acid is the sole product.

It may therefore be concluded that no profound difference in structure exists between the hydrocarbon nuclei in camphorsulphonic and camphorsulphinic acids; indeed, the method of preparation of the latter scarcely leaves room for doubt on this question. There is another circumstance which might account for the abnormal rotatory power of camphorsulphinic acid, namely, the presence in the latter substance of the enolic structure; but as yet we have not been able to find reason for supposing that such is the case, and hence for the present we incline to the view that the large change in rotation in passing from the sulphonic to the sulphinic acid is due merely to the change of sulphur from the sexavalent to the quadrivalent state. At the same time it is worthy of notice that Lowry and Donnington (*loc. cit.*) found the corresponding mercaptan, camphor-β-thiol, to possess a dextrorotatory power.

EXPERIMENTAL.

Camphor-β-sulphonic Chloride.—We have found it most convenient to prepare this substance by the action of thionyl chloride on the sulphonic acid; this method gives better yields and occupies less time than the older plan of treating the ammonium salt with phosphorus pentachloride. Camphor-β-sulphonic acid is mixed with excess of thionyl chloride, and the liquid mass heated on the water-bath until the reaction is over. The mixture is then poured into water and treated in the usual way. The yield of sulphonic chloride is almost theoretical. The product melts at 67—68°, and gives $[\alpha]_D + 30{\cdot}0°$, when $T = 22°$ and $c = 9{\cdot}998$ and $l = 1$ dcm.

Camphor-β-sulphinic Acid.—The zinc salt of this acid was prepared by the action of zinc dust on the above chloride. The zinc dust employed was obtained by treating the ordinary material with a strongly ammoniacal solution of ammonium chloride; it was then filtered and well washed, firstly with dilute spirit, and finally with absolute alcohol under which it was stored.

To prepare the zinc camphorsulphinate, 20 grams of carefully dried camphor-β-sulphonic chloride are added in portions to excess of zinc dust suspended in about 200 c.c. of absolute alcohol. After each addition of the chloride, the temperature of the mixture rises rapidly, and care should be taken to allow the reaction to subside before adding a fresh portion. When all the chloride has been added the mixture is set aside for about two hours and then filtered. The bulk of the alcohol is distilled from the filtrate, and the residue is mixed with cold water and again filtered, this time through a wet filter paper to get rid of a viscous oil which separates. The zinc dust which is left behind at the first filtration is also extracted with cold water, and finally the united aqueous filtrates are warmed on the water-bath. If too much water has not been used, the zinc salt crystallises from the hot liquid; on the other hand, some evaporation may be necessary before separation occurs. The yield is usually 10 grams, or about 47 per cent. of the theoretical, but in some experiments it was as high as 70 per cent.

Zinc camphor-β-sulphinate is very readily soluble in cold water and sparingly so in the hot medium; when cold aqueous solutions are warmed, the salt separates in clusters of long needles which do not contain water of crystallisation. The recrystallised salt was dried in a vacuum and analysed, with the following results:

1·5090 gave 0·2417 ZnO. Zn = 12·87.

0·2253 ,, 0·3981 CO_2 and 0·1332 H_2O; C = 48·19; H = 6·57.

0·2190 ,, 0·2072 $BaSO_4$. S = 12·99.

$C_{20}H_{30}O_6S_2Zn$ requires Zn = 13·13; C = 48·48; H = 6·67; S = 12·93 per cent.

Investigation of the rotatory power of the substance yielded the following data. In aqueous solution, a_D was found to be $-5·46°$ when $c = 4·000$, $T = 19°$, and $l = 2$ dcm.; hence $[a]_D$ $-68·25°$ and $[M]_D$ $-337·8°$; a_D was $-2·74°$ when $c = 2·000$, $T = 19°$, and $l = 2$ dcm.; hence $[a]_D$ $-68·5°$ and $[M]_D$ $-338·8°$; a_D was $-1·36$ when $c = 1·000$, $T = 19°$, and $l = 2$ dcm.; hence $[a]_D$ $-68·0$ and $[M]_D$ $-336·6°$.

For comparison with the above, a specimen of zinc camphor-β-sulphinate was examined in aqueous solution:

a_D $+0·61°$ when $c = 2·001$, $T = 19°$, and $l = 2$ dcm., whence $[a]_D$ $+15·24°$ and $[M]_D$ $+80·3°$; and a_D $+0·27°$, when $c = 1·0008$, $T = 19°$, and $l = 2$ dcm., whence $[a]_D$ $+13·5°$ and $[M]_D$ $+71·1°$.

The acid may be prepared by acidifying with dilute sulphuric acid an aqueous solution of the zinc salt; the precipitated oil is then extracted with ether. After drying the ethereal solution with anhydrous sodium sulphate the ether is removed by distillation. The oily residue, when set aside in a vacuum for some hours, solidifies to a colourless mass of needles.

Camphor-β-sulphinic acid crystallises in feathery needles which melt at 63—64°, and are readily soluble in cold water, alcohol, and ether.

Analysis of the substance gave the following results:

0·1936 gave 0·3915 CO_2 and 0·1297 H_2O. C = 55·15; H = 7·44.

$C_{10}H_{16}O_3S$ requires C = 55·56; H = 7·40 per cent.

The acid was also examined in the polariscope, with the following result:

a_D $-2·34°$ when $c = 1·606$, $T = 19°$, and $l = 2$ dcm., hence $[a]_D$ $-72·7°$ and $[M]_D$ $-157·2°$.

Sodium camphor-β-sulphinate was prepared by exactly neutralising a solution of the free acid with pure sodium hydroxide. The solution was evaporated on the water-bath, and the crystalline mass, after being freed from mother liquor by filtration, was dried on a porous tile. This salt forms colourless prisms which are very soluble in cold water and alcohol.

0·4630 gave 0·1262 Na_2SO_4. Na = 8·85.

$C_{10}H_{15}O_3SNa,H_2O$ requires Na = 8·98 per cent.

The rotatory power of the substance was also investigated, when it was found that in aqueous solution a_D $-1·03°$ when $c = 0·885$ (anhydrous substance), $T = 19°$, and $l = 2$ dcm.; hence $[a]_D$ $-58·2°$ and $[M]_D$ $-138·5°$.

For comparison with this an aqueous solution of sodium camphor-β-sulphonate was examined:

α_D +0·72° when $c = 2·00°$; $T = 23°$; and $l = 2$ dcm., whence $[\alpha]_D$ +18·0°, and $[M]_D$ +45·7°.

Silver camphor-β-sulphinate forms colourless prisms which are soluble in water; it also reacts readily with methyl iodide, forming colourless oils evidently sulphones, but these were not closely investigated.

The sulphinic acid reacts readily with nitrous acid, yielding a well-defined substance which crystallises in blunt, colourless prisms of melting point 137—138°. This substance, however, is not of the type $(RSO_2)_2N·OH$ normally produced from a sulphinic acid and nitrous acid, as will be readily seen from the following analytical results:

0·1647 gave 0·3478 CO_2 and 0·1073 H_2O. C = 57·5; H = 7·2.
0·1429 „ 0·3015 CO_2 „ 0·0974 H_2O. C = 57·5; H = 7·5.
0·1655 „ 0·1300 $BaSO_4$. S = 10·77.
$C_{20}H_{31}O_7NS_2$ requires C = 52·0; H = 6·7; S = 13·9 per cent.

We have not further investigated the nature of this substance.

Oxidation of Camphor-β-sulphinic Acid.—An acidified aqueous solution of zinc camphor-β-sulphinate is readily oxidised by dilute potassium permanganate at the ordinary temperature. The reaction was first investigated quantitatively. A solution of the zinc salt was acidified with dilute sulphuric acid and then titrated with *N*/10 permanganate:

0·2498 zinc salt required 19·1 c.c. *N*/10 $KMnO_4$,
0·6633 „ „ „ 48·9 „ „ „

whence 1 gram-molecule of zinc salt requires 30·3 and 29·2 grams of oxygen.

$C_{20}H_{30}O_6S_2Zn$ requires 32 grams of oxygen for conversion into sulphonate.

According to these experiments the oxygen used by the zinc salt is rather less than that required by theory for the complete conversion of sulphinic acid to the sulphonic acid, and this discrepancy is due to the formation of the α-disulphone from two molecules of sulphinic acid by the action of one atom of oxygen.

The oxidation was then carried out with a larger quantity of material. The zinc salt was dissolved in water and acidified with dilute sulphuric acid as before. Excess of aqueous potassium permanganate was then gradually poured in while the mixture was well stirred. When all the permanganate had been added the solution was set aside a short time and then treated with sulphurous acid to decompose the excess of permanganate and to remove oxides of manganese from the precipitate. The colourless crystalline precipitate was then collected by the aid of the pump.

The Soluble Portion of the Oxidation Product.—The solution was made alkaline with ammonia and the precipitated oxides of manganese removed by renewed filtration. The liquid was then evaporated to dryness on the water-bath and the residue broken up before being thoroughly dried.

This was mixed with a large excess of thionyl chloride and when the violent reaction had subsided the mixture was warmed on the water-bath for half an hour. The liquid mass was then decomposed with ice and the acid chloride which separated was filtered and finally crystallised from light petroleum. The product crystallised in leaflets which melted at 68° and when examined in the polariscope gave the following figures: A chloroform solution gave α_D $+2{\cdot}97°$ when $c=10{\cdot}023$; $T=24°$; and $l=1$ dcm.; whence $[\alpha]_D$ $+30{\cdot}4°$.

The substance is therefore the chloride of camphor-β-sulphonic acid. Armstrong and Lowry (Trans., 1902, **81**, 1447) give the melting point of this substance as 67—68° and $[\alpha]^D_{18}$ $+31{\cdot}1°$. Hence the soluble portion of the oxidation product is camphor-β-sulphonic acid.

The Insoluble Portion of the Oxidation Product. d-*Camphoryl-α-disulphone.*—The insoluble product of oxidation was recrystallised from hot alcohol, from which it separated in colourless prisms. These melt at 158° and are insoluble in cold water, sparingly so in cold alcohol, and readily so in chloroform, benzene, or glacial acetic acid:

0·2074 gave 0·4202 CO_2 and 0·1287 H_2O. C = 55·74; H = 6·89.

0·1689 „ 0·1892 $BaSO_4$. S = 15·38.

$C_{20}H_{30}O_6S_2$ requires C = 55·81; H = 6·97; S = 14·88 per cent.

A solution of the substance in chloroform was examined in the polariscope and α_D $+0{\cdot}62°$ when $c=2{\cdot}028$; $T=22°$; and $l=$ dcm.; hence $[\alpha]_D$ $+30{\cdot}6°$ and $[M]_D$ $+131{\cdot}6°$.

Cryoscopic determinations of the molecular weight gave the following results:

In glacial acetic acid:

0·2300 dissolved in 14·40 acetic acid gave $\Delta=0{\cdot}134°$; whence mol. wt. = 441.

In benzene:

0·2163 in 14·01 solvent gave $\Delta=0{\cdot}185°$; whence mol. wt. = 409.

$C_{20}H_{30}O_6S_2$ requires molecular weight = 430.

The crude material dissolves in a mixture of sulphuric acid and phenetole, giving a blue colour; this is no doubt due to the presence of traces of the sulphinic acid. The pure substance does not show this reaction.

Boiling water attacks camphor-α-disulphone very slowly, and after prolonged action shows a faintly acid reaction to litmus. The substance is sparingly soluble in cold alkali hydroxide, but dissolves more readily in the warm reagent, forming the alkali salts of camphorsulphonic and sulphinic acids. Thus a sample of the disulphone was warmed on the water-bath with a dilute solution of pure sodium hydroxide until all had dissolved. The solution was then acidified with dilute sulphuric acid and extracted with ether. The aqueous portion, after being neutralised, was evaporated to dryness and the residue extracted with absolute alcohol. This was filtered and the filtrate evaporated to crystallisation. The product was examined in the polariscope, and in aqueous solution the following numbers were obtained: $\alpha_D + 0{\cdot}15°$ when $c = 0{\cdot}868$; $l =$ 1 dcm.; and $T = 22°$; whence $[\alpha]_D$ $+17{\cdot}28$ and [M] (calculated for sodium camphor sulphonate) $+43{\cdot}9°$. The specific rotation of sodium *d*-camphorsulphonate was found (p. 524) to be $+18{\cdot}0°$ and $[M]_D$ $+45{\cdot}7°$.

The ethereal extract from the acidified solution was evaporated and the residue, after being purified, melted at 62—63° and gave the characteristic reaction of a sulphinic acid with phenetole and concentrated sulphuric acid.

The disulphone is also attacked by ammonia, yielding the anhydramide of camphor-β-sulphonic acid. Camphor-α-disulphone was warmed on the water-bath with strong aqueous ammonia for half an hour. The solution was then cooled and the crystalline precipitate was then collected and purified by recrystallisation from hot alcohol. It melted at 223°. A sample of camphor-β-sulphonic anhydramide prepared according to Armstrong and Lowry's method (Trans., 1902, 8, 1448) melted at the same temperature and a mixture of the substances from the two sources also showed the same melting point.

Roughly, quantitative experiments on the oxidation of the zinc sulphinate by the foregoing method showed that about 12 per cent. of the sulphinic acid is converted to sulphone and the remaining 88 per cent. to the sulphonic acid. The oxidation was also carried out in glacial acetic acid solution, when it was found that the amount converted to sulphone was rather higher, being about 18 per cent. of the original sulphinic acid. If the oxidation is carried out in alkaline solution no disulphone is formed.

Condensation of Camphor-β-sulphinic Acid with Anisole and Phenetole. Camphoryldianisylsulphonium.—Anisole was added gradually to a cold solution of zinc camporsulphinate in concentrated sulphuric acid. Immediately on adding the first portion of anisole the liquid assumed a deep blue colour, which disappeared as soon as excess of the phenolic ether was present and the whole of the sulphinic acid had been converted to the sulphonium base. After the mixture had been poured into a relatively large bulk of water the excess of anisole was removed by shaking with ether. At this stage alcohol was added to the aqueous layer to dissolve a small quantity of sulphonium sulphate which had separated as an oil. The solution was then treated with excess of barium hydroxide to remove the large excess of sulphuric acid, and the filtrate from the barium sulphate was saturated with carbon dioxide to remove barium and zinc. The carbonates of barium and zinc were then filtered and the liquid, which now contained the base as carbonate, was acidified with hydrochloric acid and precipitated with platinic chloride. In this way *camphoryldianisylsulphonium platinichloride* was obtained as a buff-coloured, insoluble precipitate. It was purified by precipitation with water from solution in acetone. After being dried in the steam oven the substance melted at 166° with profound decomposition :

0·1883 gave 0·0301 Pt. Pt = 15·99.

0·1603 „ 0 2806 CO_2 and 0·0707 H_2O. C = 47·74 ; H = 4·90.

$(C_{24}H_{29}O_3ClS)_2,PtCl_4$ requires C = 47·92 ; H = 4·83 ; Pt = 16·22 per cent.

The rotatory power of the substance was investigated. It was found that a solution in epichlorohydrin gave : α_D $-1·04°$, when $c = 2·009$, $T = 22°$ and $l = 1$ dcm. ; hence $[\alpha]_D$ $-51·8°$ and $[M]_D$ $-627·8°$.

The *dichromate* of camphoryldianisylsulphonium was obtained as a yellow, flocculent precipitate by adding an aqueous solution of the sulphate to an acid solution of potassium chromate. The precipitate was filtered and purified by redissolving in acetone and pouring this solution into concentrated aqueous potassium dichromate. The substance, when pure, forms an orange coloured, amorphous powder which melts with decomposition at 110° and is insoluble in water, sparingly soluble in alcohol and extremely so in acetone or epichlorohydrin :

0·2460 yielded on ignition 0·0381 Cr_2O_3. Cr = 10 60.

$(C_{24}H_{29}O_3S)_2,Cr_2O_7$ requires Cr = 10·30 per cent.

Camphoryldiphenetylsulphonium.—The platinichloride of the base was obtained by a method precisely similar to that given above for the anisyl derivative.

Camphoryldiphenetylsulphonium platinichloride is a very light brown, crystalline powder which melts at 152° and is insoluble in water but very soluble in epichlorohydrin :

0·1570 gave 0·2848 CO_2 and 0·0754 H_2O. C = 49·48 ; H = 5·34.

0·1803 „ 0·0278 Pt. Pt = 15·42.

0·2288 „ 0·0357 Pt. Pt = 15·60.

$(C_{26}H_{33}O_3ClS)_2,PtCl_4$ requires Pt = 15·5 ; C = 49·60 ; H = 5·25 per cent.

When this substance was examined in the polariscope in epichlorohydrin solution: α_D $-1.16°$ when $c=2.023$, $T=28°$ and $l=1$ dcm.; hence $[\alpha]_D$ $-57.3°$ and $[M]_D$ $-726°$.

The *dichromate* of the base forms an unstable, orange powder which melts with decomposition at 114°:

0·1892 gave 0·0277 Cr_2O_3. Cr = 10·02.
$(C_{26}H_{33}O_3S)_2,Cr_2O_7$ requires Cr = 9·76 per cent.

In conclusion, we desire to express our most hearty thanks to Professor Collie for the interest he has taken in the above experiments.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE,
LONDON.

LII.—*Derivatives of Multivalent Iodine. Part III. The Action of Heat on Iodobenzene Dichloride, and on the* m- *and* p-*Nitro- and* p-*Chloro-derivatives.*

By WILLIAM CALDWELL and EMIL ALPHONSE WERNER.

IN his original paper on the preparation of iodobenzene dichloride (*J. pr. Chem.*, 1886, [ii], **33**, 154) Willgerodt states that the compound decomposes at 115—120° with evolution of all the chlorine in the free state, leaving iodobenzene. The same change, he states, takes place when the substance is kept over sulphuric acid.

Later (*Ber.*, 1893, **25**, 3494) he remarks that the dichloride, when exposed to moist air, decomposes with evolution of hydrogen chloride. More recently (*Ber.*, 1898, **31**, 1136) F. Keppler has shown that the compound when kept in sealed tubes, even in the dark, decomposes with formation of *p*-chloroiodobenzene.

The results which we have obtained from a study of the action of heat on the three isomeric iodotoluene dichlorides have induced us to re-examine the behaviour of the iodobenzene derivative.

We find that the dichloride, when heated, undergoes sudden decomposition at temperatures varying from 110—136°, according to the rate of heating, and the main change takes place in accordance with the equation:

$$C_6H_5\cdot ICl_2 = C_6H_4ClI(1:4) + HCl.$$

The amount of chlorine evolved in the free state does not exceed 27 per cent. of the theoretical. Rapid heating favours the formation of *p*-chloroiodobenzene, which is the sole substitution derivative produced.

When iodobenzene dichloride is kept in a closed vessel or over sulphuric acid, no chlorine is evolved in the free state. It has already been shown (Werner, Trans., 1906, **89**, 1632) that *o*-iodonitrobenzene dichloride when heated loses all its chlorine in the free state, and this we find is also true in the case of the *p*-derivative; *m*-iodonitrobenzene dichloride, on the other hand, decomposes at 103° with formation of a substitution product to the extent of 27 to 28 per cent. of the theoretical. *p*-Chloroiodobenzene forms a dichloride which decomposes at 112°, a substitution derivative being formed in this case also to the extent of about 27 per cent. of the theoretical. Thus, whilst the nitro-group in *o*- and *p*-positions completely prevents the formation of a substitution product, its presence in the *m*-position has the same inhibiting effect as the chlorine atom in the *p*-position.

EXPERIMENTAL.

Action of Heat on Iodobenzene Dichloride, $C_6H_5{\cdot}ICl_2$.—The results of two experiments in which 2 grams of this substance were heated in the manner described in our previous paper are as follows:

		First traces of Cl evolved.	Sudden decomposition Cl + HCl evolved.	Percentage of Free Cl evolved.	Percentage of the theoretical for Cl_2.
Experiment I.	Heated slowly ...	102°	124°	6·97	27·0
,, II.	,, rapidly ..	87°	136—137°	5·99	23·2

The numbers in the last column represent the percentage decomposition in accordance with the equation:

$$C_6H_5{\cdot}ICl_2 = C_6H_5I + Cl_2,$$

proving that a large proportion of a substitution product is formed.

In order to examine the products of decomposition, 112 grams of iodobenzene dichloride were decomposed by heat. The liquid product obtained was shaken with potassium hydroxide solution and finally dried over the solid hydroxide. It weighed 90 grams, and after several distillations was ultimately separated into four fractions.

Fractions I, 180—195°, and II, 195—210°, consisted of iodobenzene, 26 and 21 grams respectively.

Fraction III, 210—225°, consisted of a mixture in equal proportions of iodobenzene and chloroiodobenzene, 7 grams.

Fraction IV, 225—236°, solidified on cooling to a crystalline mass, and was *p*-chloroiodobenzene, m. p. 55·5°, 20 grams.

The composition of fractions II and III was determined by chlorination and subsequent analyses of the dichlorides. Allowing for the loss accompanying the distillations, the proportion of *p*-chloroiodobenzene produced was much less than when small quantities of the iodobenzene dichloride were decomposed.

Action of Chlorine on p-*Chloroiodobenzene.*—Twelve grams of *p*-chloroiodobenzene were dissolved in chloroform, and chlorine was passed into the cold solution. There was no liberation of iodine. The *dichloride* separated in pale yellow, microcrystalline needles. It was filtered by the aid of the pump, washed with chloroform, and dried in the air. Ten grams were obtained.

0·5 gave, on trituration with potassium iodide solution,

$$Cl, 0{\cdot}11733 = 23{\cdot}46.$$

$$C_6H_4Cl{\cdot}ICl_2 \text{ requires } Cl = 22{\cdot}91 \text{ per cent.}$$

Action of Heat on p-*Chloroiodobenzene Dichloride*, $C_6H_4Cl{\cdot}ICl_2$.—Two grams were heated in the manner already described. At 83° the first trace of chlorine was evolved, and at 112° decomposition took place with effervescence, some hydrogen chloride being evolved.

$$Cl \text{ evolved}, 0{\cdot}33145 = 16{\cdot}57 \text{ per cent.}$$

This corresponds to 72·32 per cent. of the theoretical decomposition in accordance with the equation:

$$C_6H_4Cl{\cdot}ICl_2 = C_6H_4ClI + Cl_2.$$

A substitution product is formed to the extent of 27 to 28 per cent. of the theoretical.

Action of Heat on m-*Iodonitrobenzene Dichloride*, $NO_2{\cdot}C_6H_4{\cdot}ICl_2$.—The *m*-iodonitrobenzene was purified by distillation in steam. It was obtained in pale yellow crystals melting at 38·5°.* The dichloride forms glistening plates, resembling iodoform in appearance.

Two grams heated with the previously described precautions evolved chlorine at 65—66°. At 103° sudden decomposition took place with effervescence, some hydrogen chloride being evolved.

$$Cl \text{ evolved}, 0{\cdot}3233 = 16{\cdot}165 \text{ per cent},$$

which corresponds to 72·88 per cent. of the theoretical decomposition in accordance with equation:

$$NO_2{\cdot}C_6H_4{\cdot}ICl_2 = NO_2{\cdot}C_6H_4I + Cl_2;$$

consequently a substitution product is also formed, in this case to the extent of 27 to 28 per cent. of the theoretical.

Action of Heat on p-*Iodonitrobenzene Dichloride*, $NO_2{\cdot}C_6H_4{\cdot}ICl_2$.—Two grams were heated as above described. Evolution of chlorine commenced at 106°, and continued gradually up to 173°, at which temperature the product melted without any effervescence.

$$Cl \text{ evolved}, 0{\cdot}4431 = 22{\cdot}15.$$

Theory for the loss of two atoms of chlorine = 22·18 per cent.

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* The melting point is recorded as 34° (Griess) and 36° (Körner).

The decomposition in this instance is therefore complete, and confirms the result obtained by Willgerodt. During the heating the *p*-iodonitrobenzene sublimes in beautiful, long, slender, pale yellow needles.

UNIVERSITY CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN.

LIII.—*Depression of the Freezing Point of Aqueous Solutions of Hydrogen Peroxide by Potassium Persulphate and other Compounds.*

By THOMAS SLATER PRICE, D.Sc.

IN a recent paper (Trans., 1906, 89, 1092), Friend has adduced evidence supporting the idea that when hydrogen peroxide and potassium persulphate are brought together in solution an unstable compound is formed; this compound slowly decomposes, liberating oxygen and forming potassium bisulphate. If such a compound is formed, potassium persulphate should cause a less molecular depression of the freezing point of solutions of hydrogen peroxide than it does of water, assuming that a solution of hydrogen peroxide does not possess a less dissociating power than pure water. Calvert (*Ann. Physik.*, 1900, [iv], 1, 483) has shown that the dielectric constant of hydrogen peroxide is greater than that of water, and therefore, according to the Nernst-Thomson rule, the dissociating power of the former should be greater than that of the latter; this rule, however, is not valid in every case. Jones and Murray (*Amer. Chem. J.*, 1903, 30, 205), from their results for the freezing points of solutions containing both hydrogen peroxide and sulphuric acid, conclude that hydrogen peroxide has a greater dissociating power than water.

In what follows, an account is given of experiments on the freezing points of solutions in hydrogen peroxide of not only potassium persulphate, but also of potassium sulphate, sulphuric acid, and potassium hydrogen sulphate.

Method of Experiment.—The freezing point determinations were all carried out with the ordinary Beckmann apparatus, the usual precautions being observed. Since hydrogen peroxide is catalytically decomposed by platinum, a glass stirrer was used in the place of the ordinary platinum one. It was not considered necessary to make corrections for the amount of ice crystallising out, and care was taken that the supercooling was not greater than 0·5°.

The solutions were made up by volume, so that the molecular depressions refer to the lowering of the freezing point caused by 1 mol. of the solute in 1000 c.c. of the solution.

The strengths of solutions containing hydrogen peroxide were estimated by means of potassium permanganate, both before and after the freezing point determinations; usually there was no appreciable alteration in strength.

A comparison of the results for the molecular depressions of the pure substances with the results of other observers, as given in the last edition of *Physikalisch-chemische Tabellen*, will show that the agreement is satisfactory, with the exception of the values for the intermediate concentrations of sulphuric acid. If a curve is drawn through the results of other observers it will be seen that there is evidently a mistake in the value 3·98° for the molecular depression caused by 3·923 grams of sulphuric acid in 100 c.c. solution (Jones and Getman, *Amer. Chem. J.*, 1902, **27**, 436), and this causes a deviation of approximately 0·1° in some cases, as shown by the following figures:

Gm. H_2SO_4 in 100 c.c. solution......	2·180	3·052	6·539	8·720
Mol. Δ (obs.)	3·90	3·83	3·99	4·17
Mol. Δ (calc.)	3·86	3·92	4·09	4·16

The figures for the molecular depression (mol. Δ) given in the last line have been obtained from the curve drawn through the results of other observers (Loomis, Jones, Mackay, &c.).

Hydrogen Peroxide and Potassium Persulphate.

$K_2S_2O_8$ in grams.	H_2O_2 in grams.	Mol. Δ	$\Delta_1(K_2S_2O_8)$.	$\Delta_2(H_2O_2)$.	$\Delta_1 + \Delta_2$. (calc.).	$\Delta(K_2S_2O_8 + H_2O_2)$ obs.	Diff.
1·696	—	4·77° *	0·298°	—	—	—	—
1·696	3·303	4·30	0·298	1·840°	2·138°	2·110°	−0·028°
1·696	4·925	3·73	0·298	2·809	3·107	3·043	0·064
1·696	6·523	3·33	0·298	3·837	4·135	4·046	0·089

* The molecular depression when calculated as grams solute per 1000 grams water is 4·71°. Müller (*Zeitsch. physikal. Chem.*, 1893, **12**, 557) gives 4·7° for a solution containing 1·0432 grams $K_2S_2O_8$ in 100 grams of water.

(The figures in the first two columns give the weights of the respective compounds contained in 100 c.c. of the solution. Mol. Δ is the molecular depression of the hydrogen peroxide solution, caused by solution of the persulphate in it. Δ_1 and Δ_2 are the observed depressions of the freezing point of water for solutions the strengths of which are given in the first two columns. The last column gives the differences between the calculated and observed values shown in columns 6 and 7. The same arrangement is adopted in all the succeeding tables.)

The results for mol. Δ show that some combination does take place between the molecules of potassium persulphate and hydrogen peroxide when in solution together; as the concentration of the latter compound is increased the extent of combination also increases. This is perhaps better illustrated by the figures in the last five columns. In the case of a solution containing two solutes, the lowering of the freezing point of the solvent is generally approximately equal to the sum of the lowerings which each solute would separately cause. If this is not the case, the two solutes interact, and either some molecules disappear or more are formed; in the first case, the depression is less than, and in the second case greater than, the sum of the separate depressions. The figures given in the last column show that the first case is true.

Friend (Trans., 1906, **89**, 1092) has shown that potassium persulphate and hydrogen peroxide interact slowly. This would also account for the decrease in the molecular depression, if the action were appreciable. Measurements of the concentration of the hydrogen peroxide before and after the freezing point determination showed that no decomposition had taken place.

In a previous paper (Trans., 1906, **89**, 53) the author has shown that the formula of potassium permonosulphate is $KHSO_5$. One would therefore expect this salt to be formed by the interaction of potassium bisulphate and hydrogen peroxide, according to the equation $KHSO_4 + H_2O_2 = KHSO_5 + H_2O$. Freezing point determinations were therefore undertaken to see if there was any combination in solution. Before investigating this system, however, measurements were made on the systems containing the compounds from which potassium bisulphate is formed.

Hydrogen Peroxide and Sulphuric Acid.

H_2SO_4 in grams.	H_2O_2 in grams.	Mol. Δ.	$\Delta_1(H_2SO_4)$.	$\Delta_2(H_2O_2)$.	$\Delta_1 + \Delta_2$ (calc.).	$\Delta(H_2SO_4 + H_3O_2)$ obs.	Diff.
2·180	—	3·90°	—	—	—	—	—
2·180	1·621	4·11	0·866°	0·891°	1·757°	1·805°	+0·048°
2·180	2·399	4·32	0·866	1·321	2·187	2·280	0·093
2·180	3·258	4·37	0·866	1·806	2·666	2·771	0·105
3·052	—	3·83°	—	—	—	—	—
3·052	1·659	3·97	1·191°	0·917°	2·108°	2·151°	+0·043°
3·052	2·523	4·17	1·191	1·392	2·583	2·690	0·017
3·052	3·277	4·29	1·191	1·846	3·037	3·181	0·144
4·360	—	3·86°	—	—	—	—	—
4·360	1·670	4·08	1·717°	0·922°	2·639°	2·736°	+0·097°
4·360	2·480	4·25	1·717	1·331	3·098	3·271	0·173
4·360	3·336	4·38	1·717	1·860	3·577	3·809	0·232

It will be noticed that the molecular depression of the freezing point caused by sulphuric acid is increased in hydrogen peroxide solutions; the greater the concentration of the latter, the greater the increase in the molecular depression. In accordance with this the differences in the last column are positive. This confirms the results of Jones and Murray (*Amer. Chem. J.*, 1903, 20, 205), who explain them by the assumption that a solution of hydrogen peroxide possesses a greater dissociating power than pure water. This, at present, seems to be the only feasible explanation, since any action between sulphuric acid and hydrogen peroxide, according to the equation $H_2SO_4 + H_2O_2 = H_2SO_5 + H_2O$, would decrease the number of molecules having an effect on the freezing point of water, and thus bring about a decrease in the molecular depression. Moreover, permonosulphuric acid does not appear to be formed at these dilutions, at all events within the time of experiment.

It follows that the formation of the compound between potassium persulphate and hydrogen peroxide proceeds to a greater extent than that indicated by the figures for the freezing points, since the increased dissociation due to hydrogen peroxide has been more than counterbalanced.

Hydrogen Peroxide and Potassium Sulphate.

K_2SO_4 in grams.	H_2O_2 in grams.	Mol. Δ.	$\Delta_1(K_2SO_4)$.	$\Delta_2(H_2O_2)$.	$\Delta_1 + \Delta_2$ (calc.).	$\Delta(K_2SO_4 + H_2O_2)$ obs.	Diff.
3·876	—	4·12°	—	—	—	—	—
3·876	1·621	3·58	0·915°	0·891°	1·806°	1·687°	- 0·119°
3·876	2·399	3·42	0·915	1·321	2·236	2·080	0·156
3·876	3·258	3·21	0·915	1·800	2·715	2·520	0·195
5·426	—	3·96°	—	—	—	—	—
5·426	1·659	3·47	1·232°	0·917°	2·149°	1·997°	– 0·152°
5·426	2·523	3·28	1·232	1·392	2·411	2·411	0·213
5·426	3·277	3·08	1·232	1·846	2·803	2·803	0·275
5·813	—	3·93	—	—	—	—	—
7·751 *	—	3·73	—	—	—	—	—
7·751	1·670	3·37	1·657	0·922	2·579	2·421	0·158
7·751	2·480	3·15	1·657	1·381	3·038	2·780	0·268
7·751	3·336	2·99	1·657	1·860	3·517	3·186	0·331

* Supersaturated solution.

(The molecular depressions obtained by other observers for the concentrations of potassium sulphate given above are 4·04°, 3·95°, 3·93°, and 3·87° respectively.)

The molecular depression decreases with increase in concentration of the hydrogen peroxide. This is in accordance with the results of Jones and Carroll (*Amer. Chem. J.*, 1902, 28, 284) for other salts, for example, potassium chloride and nitrate, ammonium sulphate.

Hydrogen Peroxide and Potassium Hydrogen Sulphate.

The various attempts which have hitherto been made to prepare a pure salt of permonosulphuric acid have not been successful. It seemed likely that the potassium salt should result from the interaction of hydrogen peroxide and potassium bisulphate, according to the equation given on p. 533, and that concentration of the solution in the presence of excess of hydrogen peroxide would lead to the deposition of the pure salt. If potassium bisulphate is dissolved in an excess of concentrated hydrogen peroxide solution (Merck's 30 per cent. by weight), and the solution allowed to stand, permonosulphate is slowly formed. Concentration of the solution in a vacuum leads at first to the deposition of clear crystals of an acid sulphate of potassium; the remainder of the solution then dries up to a white mass, which contains permonosulphate. Analysis of this residue, according to the method given in a previous paper (Trans., 1906, **89**, 53), showed it to contain about 50 per cent. of potassium permonosulphate, the remainder consisting of one of the higher acid sulphates of potassium. No indication, judging from the analytical results, was obtained of the formation of potassium persulphate ($K_2S_2O_8$). Attempts to recrystallise the residue from more hydrogen peroxide were not successful, the permonosulphate undergoing partial decomposition during the process. Nor could any method of partial precipitation from solution be found which produced a pure salt.*

In passing, it should be mentioned that a solution containing permonosulphate (and free sulphuric acid) is much more stable than is generally supposed. I possess a solution which was made from potassium persulphate two years ago, and it does not appear to have diminished much in strength, and, moreover, gives no indication of the formation of hydrogen peroxide. In another case, 10 c.c. of a solution of permonosulphate (from $KHSO_4$ and H_2O_2) were equivalent to 27·8 c.c. of a thiosulphate solution on May 23, 1906; on August 15 the titre was 27·1 c.c., and on September 14, 26·8 c.c.

Freezing point determinations were also carried out on solutions of potassium bisulphate in hydrogen peroxide. Jones and his co-workers have found that hydrogen peroxide has a greater dissociating power for acids than water has (compare the results for sulphuric acid), and, since a solution of potassium bisulphate is acid, the effect of any combination between the bisulphate and the hydrogen peroxide would be partially masked by the effect of the $H^{\bullet}$-ions. Nevertheless, there is a slight diminution in the molecular depression of the freezing point, as is shown in the following table, which gives the results of one set of observations only.

---

* Attempts to prepare pure salts of the heavier metals, such as $Ca(HSO_5)_2$, have so far not been successful.

$KHSO_4$ in grams.	H_2O_2 in grams.	Mol. Δ.	$\Delta_1(KHSO_4)$.	$\Delta_2(H_2O_2)$.	$\Delta_1 + \Delta_2$	$\Delta(KHSO_4 + H_2O_2)$.	Diff.
8·478	—	3·52°	—	—	—	—	—
8·478	1·659	3·43	2·190°	0·917°	3·107°	3·051°	−0·056°
8·478	2·523	3·41	2·190	1·392	3·582	3·512	0·070
8·478	3·277	3·40	2·190	1·846	4·036	3·961	0·075

It is noticeable that an alteration in the concentration of the hydrogen peroxide does not affect the molecular depression to any extent. The other sets of observations gave similar results.

Chemical Department,
Municipal Technical School,
Birmingham.

LIV.—*The Reduction Products of* o- *and* p-*Dimethoxybenzoin.*

By James Colquhoun Irvine, Ph.D., D.Sc., and Agnes Marion Moodie, M.A., B.Sc., Carnegie Scholar.

The relationship of compounds of the benzoin type to the parent hydrocarbon is usually ascertained by reduction to the corresponding hydrobenzoin and subsequent treatment of this product with hydrogen iodide. By this process ordinary benzoin is converted into dibenzyl, which must be regarded as the simplest corresponding hydrocarbon.

The case of substituted benzoins offers the possibility of more complex reactions of some interest, and we have made a study of the various reduction products obtained from both *o*- and *p*-dimethoxybenzoin.

o-Dimethoxybenzoin (Trans., 1901, 79, 668) was converted into the corresponding hydrobenzoin by the action of sodium amalgam, and attempts were made to reduce this compound by means of hydrogen iodide. In this case it seemed probable that the removal of the methoxyl groups from the ortho-position might lead to the union of the two benzene nuclei, with the ultimate formation of dihydrophenanthrene. A similar reduction has recently been carried out by Law (Trans., 1906, 89, 1517), who obtained 9:10-dihydroxyphenanthrene by the electrolytic reduction of hydrosalicyloin. The reaction in question was, however, unsuccessful, and recourse was finally had to Baeyer's method of reduction, the compound being distilled with zinc dust in a current of hydrogen. Contrary to expectation, the main product thus obtained was *p-dimethyltolane*, a result which is at variance with the generally accepted statement that Baeyer's method reduces aromatic oxy-compounds to the parent hydrocarbon. Although it is difficult to speculate accurately as to the progress of reactions which take place at high temperatures, we endeavoured to trace the various stages undergone in this abnormal reduction.

With the object of isolating the intermediate products, the method of reduction was somewhat modified; the zinc dust used was not freed from adherent oxide, and the distillation was conducted at the lowest possible temperature in an atmosphere of carbon dioxide. Under these conditions the methoxyl groups remained unreduced, and the principal product consisted of *o*-dimethoxystilbene:

$$MeO\cdot C_6H_4\cdot CH(OH)\cdot CH(OH)\cdot C_6H_4\cdot OMe \longrightarrow MeO\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot OMe.$$

On further reduction under the same conditions, this substance was converted into a mixture of *o*-dimethoxydibenzyl and *p*-dimethyltolane,

$$MeO\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot OMe \longrightarrow MeO\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot OMe + C_6H_4Me\cdot C{\vdots}C\cdot C_6H_4Me,$$

and the latter substance constituted the sole product when the ethane derivative was in turn reduced.

The conversion of the *o*-methoxy-compounds into the *p*-hydrocarbon is therefore effected at the last stage of the reduction, and is in all probability due to the removal of two molecules of water, and subsequent transference of the two methyl groups to the position of greatest stability.

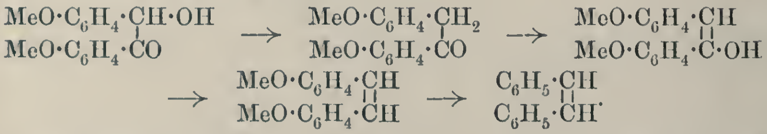
In view of the general importance of Baeyer's method of reduction and the abnormality of the above result, we extended our experiments to anisoin and its derivatives. The compounds selected for experiment were prepared with the object of testing the effect of the reduction on different side chains.

The table on page 538 classifies the results obtained.

The evidence of experiments (1) and (2) shows that the side chains $\begin{array}{l}\cdot CH\cdot OH\\ \vert\\ \cdot CO\end{array}$ and $\begin{array}{l}.CH\cdot OMe\\ \vert\\ \cdot CO\end{array}$ reduce alike to $\begin{array}{l}\cdot CH_2\\ \vert\\ \cdot CO\end{array}$, when the reduction is carried out in carbon dioxide. Moreover, experiments (3) and (4) afford additional proof that the ketonic group, and also the phenolic methoxyl groups remain unaltered under these conditions. On the other hand, reactions (5) and (6) show that the groups $\begin{array}{l}\cdot CH\cdot OH\\ \vert\\ \cdot CH\cdot OH\end{array}$ and $\begin{array}{l}CH\cdot OMe\\ \vert\\ CH\cdot OH\end{array}$, when similarly treated, reduce first to $\begin{array}{l}\cdot CH\\ \Vert\\ .CH\end{array}$. The effect of substituting hydrogen for carbon dioxide in the process is

Substance.	Conditions of experiment.	Products.
1. Anisoin	Distilled in carbon dioxide.	Deoxyanisoin ; trace of *p*-dimethoxystilbene.
2. Anisoin methyl ether.	,, ,, ,,	Deoxyanisoin ; trace of *p*-dimethoxystilbene.
3. Deoxyanisoin	,, ,, ,,	Deoxyanisoin.
4. Anisil	,, ,, ,,	Anisil.
5. Hydroanisoin	,, ,, ,,	*p*-Dimethoxystilbene.
6. Hydroanisoin monomethyl ether	,, ,, ,,	*p*-Dimethoxystilbene.
7. Deoxyanisoin...........	Distilled in hydrogen.	*p*-Dimethoxystilbene ; stilbene.
8. Hydroanisoin...........	,, ,, ,,	Stilbene.
9. *p*-Dimethoxystilbene..	,, ,, ,,	Stilbene.

shown in (7), (8), and (9), and only then is a hydrocarbon obtained. The nature of the complete reduction of anisoin, and its ultimate conversion into stilbene, is best seen if we accept the enolic formula for deoxybenzoin as shown below :



$$\begin{array}{l} MeO\cdot C_6H_4\cdot CH\cdot OH \\ MeO\cdot C_6H_4\cdot CO \end{array} \longrightarrow \begin{array}{l} MeO\cdot C_6H_4\cdot CH_2 \\ MeO\cdot C_6H_4\cdot CO \end{array} \longrightarrow \begin{array}{l} MeO\cdot C_6H_4\cdot CH \\ MeO\cdot C_6H_4\cdot C\cdot OH \end{array}$$

$$\longrightarrow \begin{array}{l} MeO\cdot C_6H_4\cdot CH \\ MeO\cdot C_6H_4\cdot CH \end{array} \longrightarrow \begin{array}{l} C_6H_5\cdot CH \\ C_6H_5\cdot CH \end{array}$$

The position occupied by the methoxyl groups in the ring therefore affects the nature of the reduction considerably. Both in the ortho- and para-compounds studied the alkyloxy-groups are evidently the last to be eliminated, but in the former case the methyl groups ultimately effect substitution in the ring, whilst in the latter they are removed, probably in the form of methyl alcohol.

Our results show that the evidence given by Baeyer's reduction process must be accepted with some caution in deducing the constitution of aromatic oxy-compounds. In particular, the irregular reduction undergone by methoxy-derivatives renders the application of this method to the determination of the structural formulæ of many alkaloids extremely doubtful.

EXPERIMENTAL.

Preparation of o-*Dimethoxyhydrobenzoin.*

The *o*-dimethoxybenzoin required was prepared, as already described (*loc. cit.*), by the condensation of salicylaldehyde methyl ether. The reduction of the compound to a hydrobenzoin was carried out by the action of sodium amalgam on a solution of the benzoin in moist ether. Ninety grams of dimethoxybenzoin were dissolved in ether saturated with water, and subjected to the action of a large excess of finely powdered 4 per cent. sodium amalgam. A brisk current of carbon dioxide was led into the well cooled solution, which was thoroughly mixed by means of a powerful mechanical stirrer. As the hydrobenzoin is practically insoluble in ether it was precipitated along with the sodium bicarbonate produced in the reaction. After forty-eight hours the liquid was filtered, and the residual sludge, after separation from mercury, was extracted with boiling alcohol. In this way the hydrobenzoin was removed, and, after recrystallisation from alcohol, was obtained in large prisms melting at 153—154°. The ethereal filtrate, on concentration, furnished an additional quantity of the powder, the total yield of which amounted to 70 grams. Analysis gave:

(I) $C = 69{\cdot}82$; $H = 6{\cdot}60$. (II) $C = 69{\cdot}92$; $H = 6{\cdot}71$.

$C_{16}H_{18}O_4$ requires $C = 70{\cdot}07$; $H = 6{\cdot}57$ per cent.

Examination showed that no products corresponding to *iso*hydrobenzoin or deoxybenzoin were produced in the reaction.

The existence of two hydroxyl groups in the hydrobenzoin was proved by boiling the compound with excess of acetic anhydride. After two hours' treatment, the excess of reagent was removed under diminished pressure, and the residue crystallised from a mixture of alcohol and light petroleum. The product, which crystallised in small prisms, melted at 171—172°, and analysis showed the substance to be the *diacetyl* derivative of the hydrobenzoin.

(I) $C = 66{\cdot}83$; $H = 6{\cdot}16$. (II) $C = 67{\cdot}15$; $H = 6{\cdot}19$.

$C_{20}H_{22}O_6$ requires $C = 67{\cdot}04$; $H = 6{\cdot}14$ per cent.

With a similar object in view, the action of phenylcarbimide on the hydrobenzoin was tried, and we obtained the *diphenylurethane* derivative in beautiful prisms (m. p. 186—187°).

Analysis gave:

$C = 70{\cdot}12$; $H = 5{\cdot}57$; $N = 5{\cdot}59$.

$C_{30}H_{28}O_6N_2$ requires $C = 70{\cdot}31$; $H = 5{\cdot}47$; $N = 5{\cdot}47$ per cent.

Reduction of o-*Dimethoxyhydrobenzoin.*—Several attempts were made in the first place to reduce the compound by means of hydrogen iodide. Experiments carried out at various temperatures ranging from 100° to 200° gave only gummy products, and even at the ordinary temperature the hydrobenzoin was rapidly converted into an uncrystallisable tar when mixed with the concentrated acid. The reduction was therefore carried out by distilling an intimate mixture of the hydrobenzoin and excess of zinc dust over pumice stone with which zinc dust was incorporated. The best yields were obtained when not more than 5 grams of the hydrobenzoin were used in each experiment. The distillation was carried out as usual in a sloping combustion tube, the end of which was fitted with an adapter dipping under alcohol. As explained in the introduction, the distillation can be controlled so as to give three distinct reduction products. When carried out at the lowest possible temperature in a stream of dry carbon dioxide, the product was an oil which, after repeated fractionation, boiled at 195—197° under 20 mm. pressure, and which did not crystallise when kept at $-10°$ for several days.

Analysis gave:

(I) C = 79·90; H = 6·58. (II) C = 80·13; H = 6·65.

$C_{16}H_{16}O_2$ requires C = 80·00; H = 6·60 per cent.

As the compound behaved as an unsaturated substance towards bromine, and was also not affected by the action of acetic anhydride, it was regarded as *o*-dimethoxystilbene. This view was confirmed by its reduction by the method just described. When distilled over zinc dust it yielded an oil which crystallised on standing. The product was purified from dilute alcohol (prisms, m. p. 83—84°).

Analysis gave:

(I) C = 79·26; H = 7·55. (II) C = 79·36; H = 7·59.

$C_{16}H_{18}O_2$ requires C = 79·34; H = 7·44 per cent.

As acetic anhydride was without action on the compound, it is considered to be o-*dimethoxydibenzyl*.

Both the above substances gave *p*-dimethyltolane when reduced by Baeyer's process, but the most convenient method of preparing the latter compound is to reduce the hydrobenzoin in a current of hydrogen. In this way the intermediate compounds in the reduction are converted into the hydrocarbon. The distillate crystallised readily on cooling, and, after draining from adherent oil on a porous plate, the crystals were purified by recrystallisation from alcohol. The product consisted of long, delicate needles melting at 136—137°, and possessing a beautiful blue fluorescence. The mother liquors from the recrystallisation invariably contained a little *o*-dimethoxydibenzyl, and the oil recovered from the porous plate proved to contain the ethylene derivative.

p-*Dimethyltolane*.—Considerable trouble was experienced in identifying the compound melting at 136—137° with *p*-dimethyltolane, as the analysis presented great difficulties. Using the ordinary combustion method, the values found for hydrogen were practically constant, but the carbon content showed great variation, ranging from 70 to 85 per cent. The admixture of copper oxide or potassium dichromate with the substance in the boat was without avail, and the substitution of the bayonet tube method was equally unsuccessful. The wet method of combustion (Fritzsche, *Annalen*, 1897, **294**, 79) and the Dennstedt process were also tried, but without success. Finally, the substance was burned in the usual way, using a tube

3 metres long. The carbon content still varied somewhat, but the results showed the compound to be a hydrocarbon. The mean value for hydrogen in twelve combustions was 6·99 per cent., and the maximum value found for carbon was 92·96 per cent. ($C_{16}H_{14}$ requires C = 93·20; H = 6·80 per cent.). The molecular weight, determined by the boiling point method in chloroform solution, was 207 (calculated 206), and the identity of the compound with *p*-dimethyltolane was further established by the preparation of the latter from *p*-dimethylstilbene dibromide. The specimen thus obtained melted, as did the compound under examination, at 136°, and a mixture of the two preparations melted sharply at the same temperature.

In view of the difficulties described above, it is a significant fact that in the original preparation of this compound (*Ber.*, 1873, **6**, 1505) no analyses are quoted.

o-*Dimethoxybenzil*.—It was considered advisable to substantiate the ortho-character of the various compounds in view of their ultimate reduction to a para-hydrocarbon. In the case of *o*-dimethoxybenzoin this has already been done (*loc. cit.*) in its conversion into *o*-methoxybenzoic acid, and similar evidence was therefore sought in the case of dimethoxyhydrobenzoin.

When boiled with alkaline potassium permanganate solution the compound underwent ready oxidation. After twelve hours' treatment the liquid was filtered, and the residue, after drying, was extracted with boiling ether. The extract on evaporation deposited a crop of well-formed, colourless prisms melting at 127°, which analysis showed to be dimethoxybenzil:

(I) C = 70·96; H = 5·31. (II) C = 71·18; H = 5·38.

$C_{16}H_{14}O_4$ requires C = 71·11; H = 5·18 per cent.

As dimethoxybenzoin gives the same product in almost quantitative amount under these conditions, the ortho nature of the hydrobenzoin is in this way confirmed. This method of preparing the benzil by the action of potassium permanganate is more advantageous than the commoner process of treatment with nitric acid, as in the latter case the by-products are not only troublesome to remove by crystallisation, but are highly explosive.

That the dimethoxybenzil was the ortho-compound was in turn confirmed by its reaction with fused potassium hydroxide. No compound corresponding to benzilic acid was formed, and the product, after acidification with hydrochloric acid, was found to contain only salicylic acid.

Reduction of Anisoin by Baeyer's Method.

This reaction was carried out exactly as already described for *o*-dimethoxyhydrobenzoin, a current of carbon dioxide being employed in the first instance. The product was an oil which crystallised completely on cooling. On recrystallisation from hot alcohol a small first crop was obtained consisting of leaflets which melted at 205—207°, but the bulk of the product, amounting to 80 per cent. of the substance used, separated in long needles. The latter compound was treated with cold ethyl acetate, and in this way freed from traces of the product of higher melting point which remained undissolved. After removal of the solvent the residue was crystallised from hot alcohol, the compound then melting at 108—109°.

Analysis showed the substance to be deoxyanisoin:

C = 75·07; H = 6·38; OMe = 26·0.

$C_{16}H_{16}O_3$ requires C = 75·00; H = 6.25; OMe = 25·6 per cent.

As Russell (*Annalen*, 1869, **151**, 25) quotes 95° as the melting point of deoxyanisoin, and as, moreover, *iso*hydroanisoin melts at 110°, the substance was further examined. The molecular weight was determined in benzene by the cryoscopic method, and gave the value 240 (calculated 256). The compound, moreover, had no action on Fehling's solution, and was recovered unchanged when boiled with either acetic anhydride or dilute sulphuric acid. When boiled with alkaline potassium permanganate it was converted into anisil (m. p. 133°). The presence of the ketonic group was shown by the action of hydroxylamine. The compound was boiled for three hours in methyl-alcoholic solution with the calculated amount of the base. The solution was poured into water, and the crystalline precipitate separated, dried, and recrystallised from a mixture of benzene and light petroleum.

Analysis of the product, which crystallised in needles melting at 120—121°, showed it to be the oxime of deoxyanisoin:

C = 70·68; H = 6·48.

$C_{16}H_{17}O_3N$ requires C = 70·85; H = 6·27 per cent.

As already mentioned, the reduction of anisoin also yielded a small quantity of a compound melting at 205—207°.

Analysis gave:

C = 79·95; H = 6·87; OMe = 26·80.

$C_{16}H_{16}O_2$ requires C = 80·00; H = 6·60; OMe = 25·83 per cent.

As, in addition, the compound gave a bromine derivative melting at 118—120°, it is evidently *p*-dimethoxystilbene.

Both deoxyanisoin and dimethoxystilbene were found to distil unchanged when heated with zinc dust in a stream of carbon dioxide, but in an atmosphere of hydrogen each compound was converted into stilbene. The latter was identified by its melting point (124°) and its conversion into *a*-stilbene dibromide (m. p. 237°).

Preparation and Reduction of Anisoin Derivatives.

Anisoin Methyl Ether.—This compound was prepared by the silver oxide method in the manner already described for the corresponding ortho-compound (*loc. cit.*). The addition of a little dry acetone was necessary to effect complete solution of the anisoin in the methyl iodide. The product crystallised readily in pale yellow prisms, which after recrystallisation from carbon tetrachloride melted at 52—53°. The yield was quantitative. The compound is very soluble in ether, acetone, or benzene; a cold saturated alcoholic solution, on heating to about 60°, deposits a portion of the dissolved compound as an oil, which, however, redissolves at higher temperatures.

Analysis gave:

C = 71·38; H = 6·26; OMe = 31·8.

$C_{17}H_{18}O_4$ requires C = 71·32; H = 6·29; OMe = 32·5 per cent.

As the compound is much more volatile than anisoin, the reduction with zinc dust had to be conducted more slowly. As already explained, the same reduction products were obtained as in the case of anisoin.

Hydroanisoin Monomethyl Ether.—The reduction of the ketonic group in anisoin methyl ether was effected by the action of sodium amalgam with the production of the corresponding hydrobenzoin methyl ether. The details of the process were the same as already described for the preparation of *o*-dimethoxyhydrobenzoin. The product crystallised in complicated prisms (m. p. 98—99°) from a concentrated solution in ethyl alcohol.

Analysis gave:

C = 70·57; H = 7·03; OMe = 31·63.

$C_{17}H_{20}O_4$ requires C = 70·83; H = 6·94; OMe = 32·29 per cent.

In this case also the reduction by Baeyer's process was carried out slowly on account of the volatility of the compound. The reduction yielded *p*-dimethoxystilbene.

Hydroanisoin.—This compound is best prepared by the action of sodium amalgam on an ethereal solution of anisoin, the separation of the product from the sodium bicarbonate being effected by extraction with absolute alcohol. The yield of pure product (m. p. 167—169°) was more than 71 per cent. of the theoretical amount, and no *iso*hydroanisoin or deoxyanisoin was produced. Reduction with zinc dust gave *p*-dimethoxystilbene as the sole product when the reaction was carried out in an atmosphere of carbon dioxide. When a current of hydrogen was used the reduction proceeded further and stilbene was the main product.

Deoxyanisoin.—We found it more convenient to prepare the necessary deoxyanisoin by the distillation of a mixture of zinc dust and anisoin in a current of carbon dioxide. The product was separated as already described from traces of *p*-dimethoxystilbene by solution in cold ethyl acetate. This method of preparation gives a better yield and purer product than that obtained by the decomposition of hydroanisoin by means of sulphuric acid.

Anisil.—The anisil required was prepared from anisoin by boiling for two hours with a solution of the calculated amount of alkaline potassium permanganate. The residue obtained on filtration was extracted with boiling ether. In this way the diketone was obtained in almost quantitative amount in pale yellow needles melting at 133°. The method possesses obvious advantages over the alternative process, in which nitric acid is used as the oxidising agent.

We are extending our work on the mechanism of Baeyer's reduction process, and have obtained further results, which we hope to publish shortly.

The scheme of this investigation was suggested by the late Johannes Wislicenus, and part of the work was carried out under his direction. Acknowledgment is also due to the Carnegie Trust for a research grant in aid of the work.

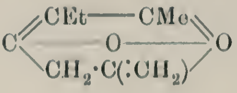
CHEMICAL RESEARCH LABORATORY,
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS.

LV.—*The Action of Ethylene Dibromide and of Propylene Dibromide on the Disodium Derivative of Diacetylacetone.*

By ALEXANDER WILLIAM BAIN.

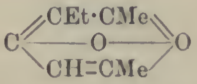
IN a previous communication (Trans., 1906, 89, 1224) the author gave a description of a compound having the composition $C_7H_8O_3Na_2,H_2O$, which he obtained by the action of ethyl iodide on the hydrated disodium derivative of diacetylacetone.

This substance, which was considered to be best represented by the formula:



$$\mathrm{C}\begin{array}{c} \diagup\!\!\diagup\,\mathrm{CEt}\!-\!\!-\!\!-\!\mathrm{CMe}\,\diagdown\!\!\diagdown \\ \mathrm{O}\!-\!\!-\!\!-\!\!-\!\!-\! \\ \diagdown\,\mathrm{CH_2{\cdot}C({:}CH_2)}\,\diagup \end{array}\mathrm{O}$$

when boiled with concentrated hydrochloric acid, is changed into dimethylethylpyrone,



Also a similar compound was obtained by the action of *n*-propyl iodide on the disodium derivative.

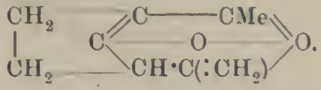
The present investigation was undertaken in order to see if analogous compounds could be obtained by the action of ethylene dibromide and propylene dibromide on the disodium derivative of diacetylacetone.

It was expected that two molecules of sodium bromide would be formed, and that rearrangement and subsequent loss of water would result in the formation of substances of similar type to that referred to above, and that the group $\cdot CH_2\cdot CH_2\cdot$ would be present in the compound obtained by the action of ethylene dibromide. This expectation has been realised, for after separation from resinous substances, which formed in considerable quantity during the course of the reaction, a pale yellow oil was obtained which distilled at 270° under a reduced pressure of 20 mm.

After standing for a few days, this oil solidified to a pale yellow solid of low melting point, which, on analysis, gave the formula $C_9H_{10}O_2$. It not only at once decolorised a solution of bromine in carbon tetrachloride without evolution of hydrogen bromide amongst other properties, but in appearance also was exactly similar to the substance prepared by the action of ethyl iodide on the disodium derivative.

The experiments made with the substance and its observed properties (see later) have suggested that its constitution may be represented by a formula having a structure as far as possible in accordance with the one referred to above.

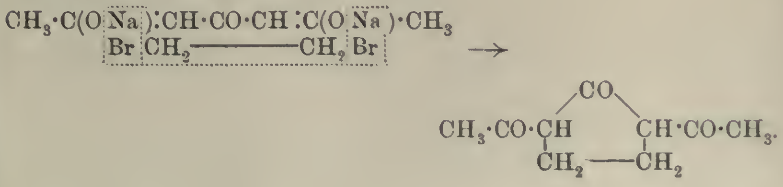
It is, therefore, proposed to write it thus:



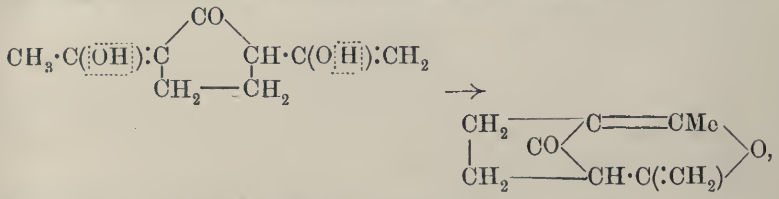
Writing the disodium derivative of diacetylacetone as

$$CH_3\cdot C(ONa){:}CH\cdot CO\cdot CH{:}C(ONa)\cdot CH_3,$$

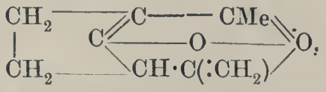
its formation may be explained as follows:



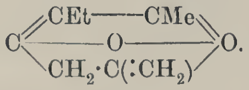
Rearrangement with the elimination of water then gives



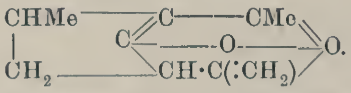
which may be written in the tautomeric form,



corresponding to that of the ethyl derivative:

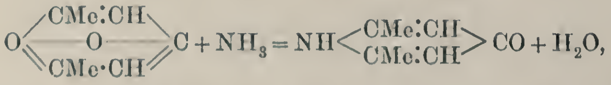


The result of the action of propylene dibromide, $CH_3{\cdot}CHBr{\cdot}CH_2Br$, on the disodium derivative was an oil which was similar to that obtained by the action of ethylene dibromide; it distilled at 274° under a reduced pressure of 20 mm., and solidified on standing to a pale yellow solid. The oil decomposes on attempting to distil it at the atmospheric pressure. On analysis it gave the formula $C_{10}H_{12}O_2$, and as it shows exactly similar properties to the ethylene derivative, presumably has a corresponding structure, but contains the group $\cdot CHMe{\cdot}CH_2\cdot$ in place of $\cdot CH_2{\cdot}CH_2\cdot$, thus:

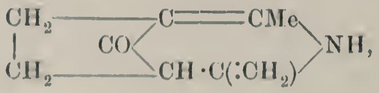


The action of trimethylene bromide on the disodium derivative of diacetylacetone resulted in the formation of a viscous substance, which on distillation, even under reduced pressure, changed to tar.

Since dimethylpyrone reacts with ammonia to form lutidone, thus:

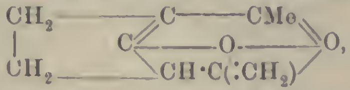


experiments were made with the view of ascertaining if a similar reaction might occur in the case of the compounds under investigation. This was found to be the case, for on heating the ethylene derivative with concentrated ammonia in a sealed tube at 140°, a pale yellow solid was obtained, which had the composition $C_9H_{11}ON$, suggestive of the structure

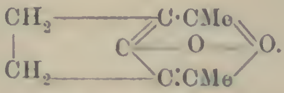


if we assume the structural formula for the ethylene derivative to be that proposed above. The existence of the $:C:CH_2$ group in these compounds was proved by oxidising with dilute chromic acid solution and distilling. The strongly acid distillate, after being neutralised with dilute sodium hydroxide solution, at once reduced an ammoniacal solution of silver nitrate, indicating that the $:CH_2$ group had been oxidised to formic acid (compare Trans., 1906, **89**, 1228).

Perhaps the most interesting property of the compound,



is that on boiling it with concentrated hydrochloric acid for several hours, it undergoes isomeric change and forms the hydrochloride of a pyrone derivative, namely:



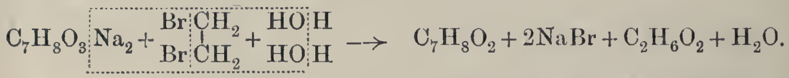
A similar change occurs when the propylene derivative is heated with concentrated hydrochloric acid. Both substances, after being thus treated, no longer give formic acid as the result of oxidation with dilute chromic acid, and resemble the alkyl derivatives of dimethylpyrone already described (*loc. cit.*) by the author.

Much difficulty was experienced before the conditions necessary for success were discovered. It would seem that an essential factor is the absence of water.

The disodium derivative of diacetylacetone has the constitution $C_7H_8O_3Na_2,2H_2O$ when prepared by dissolving dimethylpyrone in 95 per cent. alcohol and adding a solution of sodium ethoxide (the calculated quantity) also in 95 per cent. alcohol. On heating the mixture on the water-bath the above hydrated form is obtained, which is insoluble in boiling alcohol and can be separated by filtration. If this is dried on the water-bath under reduced pressure, it loses a molecule of water and becomes $C_7H_8O_3Na_2,H_2O$.

The anhydrous disodium derivative is made by acting on dry diacetylacetone (prepared from the barium salt of dimethylpyrone) suspended in dry alcohol with sodium ethoxide solution, formed by dissolving sodium in dry alcohol. The anhydrous compound, $C_7H_8O_3Na_2$, separates and can be filtered off.

In the earlier experiments the hydrated derivatives were employed, although it was feared that the presence of water might lead to disappointing yields of the desired product, as was experienced when experimenting with the alkyl iodides. This proved to be the case, since dimethylpyrone and sodium bromide were obtained in large amount as the result of the interaction of ethylene dibromide and the hydrated disodium derivatives, but very small quantities of the oil described below. This may be explained by the possibility of the hydrated derivative reacting thus:



$$C_7H_8O_3Na_2 + \begin{matrix} Br\,CH_2 \\ Br\,CH_2 \end{matrix} + \begin{matrix} HO\,H \\ HO\,H \end{matrix} \longrightarrow C_7H_8O_2 + 2NaBr + C_2H_6O_2 + H_2O.$$

When the anhydrous disodium derivative was used, fairly good yields were obtained, and this variety was employed in all the preparations subsequently made.

EXPERIMENTAL.

The Action of Ethylene Dibromide on the Disodium Derivative of Diacetylacetone.

Twenty-eight grams of the anhydrous disodium derivative, $C_7H_8O_3Na_2$, were suspended in 150 c.c. of dry alcohol and 31 grams (a slight excess) of ethylene dibromide were added; this mixture was heated on the water-bath for about five hours. A large quantity of sodium bromide separated out and the contents of the flask were neutral. The sodium bromide was separated by filtration and most of the alcohol was evaporated on the water-bath. On adding water to a portion of the remaining liquid, an insoluble oil separated out. Water was then added to the whole of the liquid: it was well shaken and extracted with chloroform and distilled under a reduced pressure of 20 mm., after removal of the chloroform.

About 6 grams of a pale yellow oil distilled at constant b. p. 270° (20 mm.), after which the thermometer rose and the remainder began to decompose at higher temperatures.

Several preparations were carried out as above and a total yield of nearly 25 grams obtained. The oil decomposed on attempting to distil it at atmospheric pressure.

A qualitative examination proved the absence of bromine in the compound. After standing for a few days it solidified, forming a pale yellow solid of a non-crystalline character, which melted between 62° and 63°. On analysis:

(1) 0·1940 gave 0·5119 CO_2 and 0·1160 H_2O. C = 71·9; H = 6·6.

(2) 0·2015 ,, 0·5310 CO_2 ,, 0·1219 H_2O. C = 71·8; H = 6·7.

$C_2H_{10}O_2$ requires C = 72·0; H = 6·6 per cent.

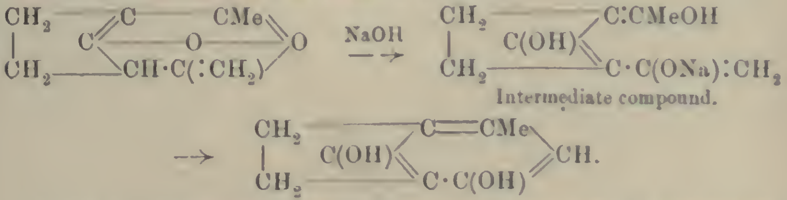
A molecular-weight determination by the boiling point method was carried out, benzene being employed as the solvent.

0·1632 of substance in 14·15 of benzene caused a rise of 0·19° in boiling point, corresponding to a molecular weight of 162; $C_9H_{10}O_2 = 150$.

The compound is insoluble in water, but dissolves easily in alcohol, chloroform, or ether, and in most organic solvents. Acetic acid readily dissolves it, but hydrochloric acid very slowly attacks it, producing isomeric change.

Ferric chloride solution gives no coloration, indicating the absence of a hydroxyl group in the molecule. All attempts to prepare an oxime and an hydrazone failed, suggesting the absence of doubly bound oxygen as a carbonyl group. The reasons for assuming the presence of the unsaturated group $:C:CH_2$ have been already given.

Action of Sodium Hydroxide.—Cold sodium hydroxide solution dissolves the substance, giving a yellow solution which becomes red on warming. When heated with sodium hydroxide, alcohol, and chloroform it gives a deep red solution, which on dilution with water shows a beautiful green fluorescence. This suggests that a derivative of orcinol may have been formed in the following manner, the five-membered ring being stable towards alkali :



Action of Hydrochloric Acid. Dimethylethylenepyrone hydrochloride, $(C_9H_{10}O_2)_2HCl,2H_2O$.—Two grams of the compound were boiled with concentrated hydrochloric acid in a flask attached to a reflux condenser for six hours. Most of it had then gone into solution and a test portion of the liquid on evaporation deposited white, needle-shaped crystals. These crystals were quite stable at the ordinary temperature, but are decomposed by water, and on being heated in a test-tube they lose water and hydrogen chloride. The remainder of the liquid was evaporated and the crystals, after being dried on a porous plate, were analysed. On titration with decinormal silver nitrate solution :

0·15 required 3·9 c.c. of the silver solution, this being equivalent to 0·01385 chlorine. Cl = 9·23.

$(C_9H_{10}O_2)_2HCl,2H_2O$ requires Cl = 9·53 per cent.

Platinichloride of Dimethylethylenepyrone, $(C_9H_{10}O_2)_2H_2PtCl_6,2H_2O$. —If platinic chloride is added to a solution of dimethylethylenepyrone in hydrochloric acid, a yellow *platinichloride* separates out on gently warming and stirring the mixture with a glass rod. This salt can be recrystallised by dissolving it in warm water, in which it is sparingly soluble, and allowing the aqueous solution to evaporate. If the solution is boiled it decomposes, giving a resinous material containing platinum. After drying on a porous tile in a desiccator, some of the compound was analysed. That the platinichloride prepared as described above possessed water of crystallisation was rendered evident by heating some in a test-tube, when water was evolved:

0·2365 gave 0·2502 CO_2, 0·0746 H_2O, and 0·0617 Pt. C = 28·8; H = 3·5; P = 26·1.

$C_{18}H_{26}O_6Cl_6Pt$ requires C = 28·9; H = 3·5; Pt = 26·1 per cent.

Action of Ammonia.—One gram of the compound was dissolved in concentrated ammonia solution and the mixture heated in a sealed tube for five hours at 135—140°. The contents of the tube were then placed in a distilling flask and distilled under reduced pressure. After the ammonia and water had passed over, about half a gram of a pale yellow oil was collected between 280° and 285° (25 mm.). This was allowed to stand for a few days in a vacuum desiccator, when it solidified to a pale yellow solid, which melted between 97° and 98°. A qualitative examination showed the presence of nitrogen. Oxidation with dilute chromic acid solution, as described above, and the action of bromine dissolved in carbon tetrachloride, afforded evidence that the $:C:CH_2$ group remained unchanged in the molecule:

0·1500 gave 0·3978 CO_2 and 0·1025 H_2O. C = 72·3; H = 7·6.
0·1250 ,, 10·4 c.c. moist nitrogen at 16° and 764 mm. N = 9·7.

$C_9H_{11}ON$ requires C = 72·5; H = 7·4; N = 9·4 per cent.

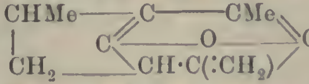
The Action of Propylene Dibromide on the Disodium Derivative of Diacetylacetone.

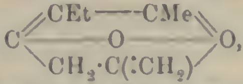
With the expectation that by employing propylene dibromide, $CH\cdot MeBr\cdot CH_2Br$, compounds would be obtained similar to those produced by the action of ethylene dibromide, several experiments were made with this substance. The method of procedure was identical with that employed in the investigation of the action of ethylene dibromide on the anhydrous disodium derivative, but a considerable excess of propylene dibromide was employed. The yields of the propylene derivative were comparatively small. Starting with 20 grams of the anhydrous disodium derivative in each preparation, only from 2 to 3 grams of a pale yellow oil were obtained, which distilled at 274° under 20 mm. pressure. The oil decomposes into a tarry product on attempting to distil it under the ordinary atmospheric pressure. After standing for a few days in a vacuum desiccator it solidified to a pale yellow solid, which melted at 66—67°. On analysis:

(1) 0·1652 gave 0·4415 CO_2 and 0·1098 H_2O. C = 72·9; H = 7·4.
(2) 0·1925 ,, 0·5154 CO_2 ,, 0·1305 H_2O. C = 73·0; H = 7·5.

$C_{10}H_{12}O_2$ requires C = 73·1; H = 7·3 per cent.

The compound is insoluble in water and resembles the corresponding ethylene derivative in all its reactions. Like this derivative, it undoubtedly undergoes isomeric change to a pyrone derivative on boiling with concentrated hydrochloric acid, since the product, after distillation with dilute chromic acid, failed to give any formic acid, as might be expected if the $:C:CH_2$ group had remained unaltered.

The formula  appears to explain satisfactorily all its reactions and has, therefore, been adopted. The action of trimethylene bromide, $CH_2Br\cdot CH_2\cdot CH_2Br$, on the disodium derivative of diacetylacetone was investigated, but repeated attempts only resulted in the formation of a brown, viscous substance containing bromine, which on distillation under 35 mm. pressure changed to tar. This substance was formed after heating a mixture of trimethylene bromide and the anhydrous disodium derivative for two days on the water-bath.

It would appear from the above experiments and from those described in the previous communication (*loc. cit.*) that both the alkyl and alkylene halides of higher molecular weight react with great difficulty with the disodium derivative of diacetylacetone and then to give very unstable compounds. The remarkable faculty for undergoing isomeric change possessed by the ethyl derivative,  when heated with acids and alkalis is also shared with the ethylene derivative described above, and these compounds well illustrate the property common to several diacetylacetone derivatives of readily condensing to form orcinol compounds. The bridged ring formulæ have been considered to best explain the reactions of these compounds, although the disodium derivative of diacetylacetone probably possesses an open chain structure (compare Willstätter and Pummerer, *Ber.*, 1905, **38**, 1461).

In conclusion, the author desires to express his best thanks to Professor Collie for the continuance of his valuable advice and suggestion during the progress of these experiments.

The Organic Chemistry Laboratory,
University College,
London.

LVI.—*Volume Changes which Accompany Transformations in the System* $Na_2S_2O_3:5H_2O$.

By Harry Medforth Dawson and Colin Gyrth Jackson.

In the course of some experiments on the lowering of the temperature at which sodium thiosulphate pentahydrate is transformed into the dihydrate, certain observations were made relative to the crystallisation of supercooled solutions which appeared to warrant a closer examination of the possible changes in the system $Na_2S_2O_3:5H_2O$.

A paper by S. W. Young and J. P. Mitchell on supercooled fusions and solutions of sodium thiosulphate (*J. Amer. Chem. Soc.*, 1904, **26**, 1389) escaped our notice until a considerable amount of experimental work had been done, and the publication of numerous solubility data has been rendered unnecessary by the appearance of the abovementioned and by a later paper by Young and W. E. Burke (*ibid.*, 1906, **28**, 315) on the hydrates of sodium thiosulphate.

On this account the present communication deals almost entirely with the observations made in the study of the volume changes which accompany transformations in the system containing 5 mols. of water per mol. of sodium thiosulphate.

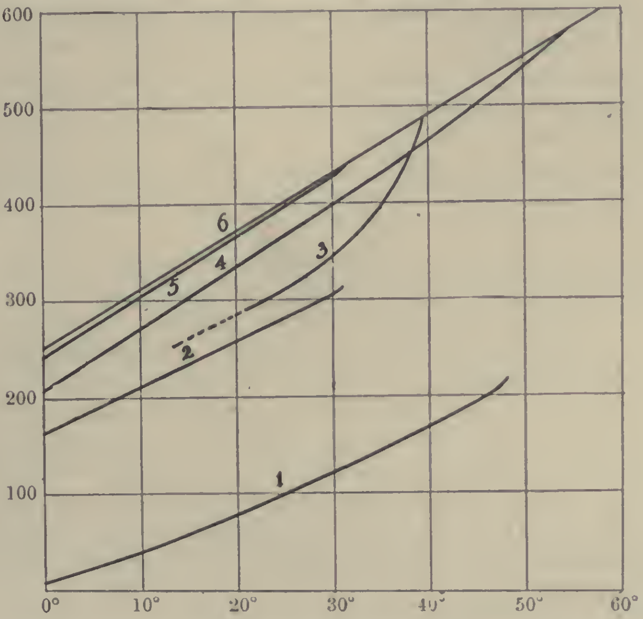
In this investigation a number of dilatometers have been subjected to a succession of temperature changes extending over many months. The dilatometers containing known quantities of recrystallised sodium thiosulphate ($Na_2S_2O_3,5H_2O$) and of heavy petroleum to serve as index fluid were heated in a thermostat, the temperature of which could be maintained constant within the limits ±0·05°. The volume of the contained system, which is read off on the graduated capillary stem of the dilatometer, varies with the nature of the component phases, and it has been found that by suitable thermal treatment the volume may at one and the same temperature assume several different, but yet perfectly defined, values.

The volume differences are most readily seen, and the conditions under which the various forms of the system have been obtained can be most easily described by reference to the appended diagram.

In this, temperatures are represented on the abscissa and dilatometer readings, the differences between which measure the changes in volume investigated, are plotted as ordinates.

In discussing the volume relationships, the very convenient nomenclature introduced by Young and Burke (*loc. cit.*) for the purpose of grouping the various hydrates of sodium thiosulphate will be used. Curve (1) in the diagram represents the volume at a series of temperatures when the system $Na_2S_2O_3:5H_2O$ is in the form of ordinary sodium thiosulphate—primary pentahydrate. When maintained for a sufficiently long time at a constant temperature above 48°, the primary pentahydrate is transformed, and either partial or complete liquefaction takes place. Which of these changes will occur under given conditions cannot be predicted. It is not entirely a question of temperature, for whereas complete liquefaction took place when the primary pentahydrate was heated at 49°, 50°, and 52°, yet at 51° the liquefaction was only partial and a small quantity of a new solid phase appeared. Furthermore, in a series of tubes containing pentahydrate which were slowly heated in a large water-bath under exactly similar conditions, superheating, resulting in complete liquefaction, was observed in about 60 per cent. of cases, partial liquefaction in the remaining 40.

Volume-temperature curves for the system $Na_2S_2O_3:5H_2O$.



On cooling the dilatometer containing the system $Na_2S_2O_3:5H_2O$ in the liquid condition, the volume temperature curve (6) was obtained.

The composition of the crystals, which appear on partial liquefaction of the primary pentahydrate, was determined by slowly evaporating a concentrated solution of sodium thiosulphate in a jacketed thermostat at a temperature of 50—55°. When crystallisation had commenced, the solution was allowed to cool slowly out of contact with the air, when large, well-formed crystals separated out. In order to remove these in a pure condition, the temperature was raised to about 55°, the mother liquor poured off, and the crystals washed with a mixture containing 80 per cent. of methyl alcohol and 20 per cent. of water which had been also heated to the same temperature. Analysis of the crystals gave numbers corresponding almost exactly with the formula $Na_2S_2O_3,2H_2O$.

On cooling the dilatometer in which crystals of this dihydrate —primary dihydrate—had formed, and shaking the contents so as to ensure the attainment of equilibrium between the solid and liquid phases at each observation temperature, the volume temperature curve (4) was obtained. Along this curve the system is represented by an equilibrium mixture of primary dihydrate and its saturated solution. The temperature of disappearance of the dihydrate, at which curve (4) intersects curve (6) was determined, in a more exact manner than is possible in the dilatometer itself, by rotating sealed tubes containing the system $Na_2S_2O_3:5H_2O$ in the form of primary dihydrate and saturated solution in a water-bath with glass sides, the temperature of this being slowly raised. In this way the two curves were found to intersect at 54°.

When the dilatometer containing supercooled liquid of the composition $Na_2S_2O_3:5H_2O$ is subjected to a temperature between −10° and −20°, complete solidification takes place and secondary pentahydrate separates in the form of long needle-shaped crystals (Parmentier and Amat, *Compt. rend.*, 1884, **98**, 735). With the system in this form the volume temperature curve (2) was obtained. There is an upper limit to this curve, for, at about 30°, partial liquefaction accompanied by increase in volume occurs and a new system, characterised by its own volume temperature curve, is formed. The composition of the hydrate resulting from the transformation of secondary pentahydrate was determined by operating in a manner similar to that employed in the separation of primary dihydrate, and the analytical data correspond with the formula $Na_2S_2O_3,4H_2O$. The new system formed at 30° is thus represented by a mixture of the tetrahydrate (secondary tetrahydrate) and its saturated solution. By raising and lowering the temperature and agitating the contents of the dilatometer to obtain equilibrium between the solid and liquid phases, the volume temperature curve (3) was realised. At 39·5° the solid phase disappears and this is the temperature at which curve (3) intersects curve (6). The portion of curve (3) below 30° corresponds with a supercooled condition. Young and Burke (*loc. cit.*) express the opinion that the system, secondary tetrahydrate and saturated solution, cannot be cooled below the temperature of formation of secondary tetrahydrate from pentahydrate, but we have on two occasions succeeded in cooling the system to 25°, thereby obtaining a perfectly definite dilatometer reading corresponding to a volume which is considerably greater than the volume of the system in the form of secondary pentahydrate.

The volume temperature curve (5) remains to be discussed. When the dilatometer containing supercooled liquid was allowed to stand at the room temperature for some days (in some cases weeks), well-formed crystals separated out slowly in small quantity. Crystals which separated under similar conditions from the same liquid contained in sealed tubes, gave on analysis numbers corresponding with the monohydrate $Na_2S_2O_3,H_2O$. The volume temperature curve for the system monohydrate and saturated solution is somewhat difficult to realise on account of the slowness with which equilibrium between the solid and liquid phases is attained. The comparatively large size of the crystals and the difficulty of agitating the contents of the dilatometer at constant temperature for long periods of time prevented the determination of the volume of the system at gradually increasing temperatures, but by cooling in ice for several days a constant reading of the dilatometer was obtained, and this gives a point on the curve (5) at 0°. By rotating sealed tubes containing the system

$$Na_2S_2O_3:5H_2O$$

in the form of monohydrate and saturated solution, the temperature of disappearance of the solid phase was found to be 31·3°, which is therefore the temperature at which curve (5) cuts curve (6).

A special interest attaches to these observations with the dilatometer in that the different forms in which the system

$$Na_2S_2O_3:5H_2O$$

can exist at a particular temperature are clearly indicated by different scale readings, each corresponding to a definite volume. At 25°, for example, the volume has been found to have at least six different values corresponding to the following forms: (1) primary pentahydrate; (2) secondary pentahydrate; (3) secondary tetrahydrate and saturated solution; (4) primary dihydrate and saturated solution; (5) secondary monohydrate and saturated solution; (6) liquid. Referred to the formula weight ($Na_2S_2O_3:5H_2O$) in grams, the volume of the system in these various forms is, 142·30, 146·38, 147·03, 148·34 (149·08), and 149·13 c.c. respectively.

According to the observations of Young and Burke (*loc. cit.*), all the possible forms of the system $Na_2S_2O_3:5H_2O$ at 25° have not been realised in our dilatometer experiments. Supercooled fusions of the pentahydrate, when cooled, are said to yield occasionally an opaque mass of crystals consisting of a mixture of hexahydrate (tertiary or quaternary) and anhydrous salt. At about 14° the hexahydrate is transformed into tertiary sesquihydrate, $2Na_2S_2O_3.3H_2O$, or into a quaternary hydrate of the composition $3Na_2S_2O_3,4H_2O$, and according to solubility data it should be possible to obtain the system $Na_2S_2O_3 : 5H_2O$ in the form of each of these hydrates and the corresponding saturated solution. A further form of the system, quaternary dihydrate and saturated solution, is also possible according to solubility data (Young and Burke, *loc. cit.*). In our experiments the formation of hexahydrate from supercooled fusions of primary pentahydrate has not been observed and the conditions for the three last-mentioned forms of the system have in consequence not been attained.

The stable form of the system below 48° is that represented by the primary pentahydrate, and in the course of the investigations the transformation of the forms (2), (5), and (6) into (1) has been observed at the room temperature. It should, however, be stated that the possibility of inoculation by nuclei was not positively excluded under the conditions of the experiments, for the dilatometers were not hermetically sealed, although the contents were effectually prevented from contact with the atmosphere by a long column of petroleum in the capillary stem of the instrument.

The transformation of secondary pentahydrate into the stable primary form affords an interesting lecture experiment. A glass tube closed at one end, 30—40 cm. long and about 1 cm. in diameter, is almost filled with the liquid obtained by heating ordinary sodium thiosulphate at 70—80°, and after being closed with a well-fitting cork is cooled in a mixture of ice and salt. The liquid solidifies completely and the resulting secondary pentahydrate presents a more or less translucent appearance. If a crystal of the ordinary hydrate is dropped into the tube, transformation of secondary into primary pentahydrate begins at once, and a considerable quantity of heat is developed. On account of the opaque appearance of the transformed mass, the surface of separation, which moves steadily down the tube, can be readily seen from a considerable distance. The opacity of the resulting primary pentahydrate is probably connected with the contraction in volume which accompanies its formation from the secondary form. Experiments are now being made to determine the velocity with which this surface of transformation is propagated under varying conditions.

The readings obtained with carefully calibrated dilatometers containing known quantities of sodium thiosulphate permit of a very accurate determination of the specific gravity of the primary and secondary pentahydrates, for the volumes of these can be directly compared with the volume of the supercooled liquid, the specific gravity of which was determined by means of a pyknometer. For the specific gravity of the primary pentahydrate the following values have been given: 1·734 (Schiff, *Annalen*, 1860, **113**, 350); 1·736 at 10° (Kopp, *Annalen*, 1855, **93**, 129); 1·729 at 17° (Dewar, *Chem. News*, 1902, **85**, 289). By extrapolation, from measurements of the specific gravity of less concentrated solutions, Schiff (*Annalen*, 1860, **113**, 188) obtained $D_{4^\circ}^{19^\circ} = 1 \cdot 6659$ for a solution of the composition

$$Na_2S_2O_3,5H_2O.$$

These numbers all appear to be too small. The values which we have obtained for $D_{4^\circ}^{20^\circ}$ are (1) liquid $Na_2S_2O_3,5H_2O$, 1·6730; (2) primary pentahydrate, 1·750; (3) secondary pentahydrate, 1·702.

THE UNIVERSITY,
LEEDS.

LVII.—*The Constitution of Chaulmoogric and Hydnocarpic Acids.*

By MARMADUKE BARROWCLIFF and FREDERICK BELDING POWER.

IN a previous communication on "The Constituents of Chaulmoogra Seeds" (Power and Gornall, Trans., 1904, **85**, 838) the isolation of a new, unsaturated, optically active acid was described. This acid, designated chaulmoogric acid, melted at 68°, had $[\alpha]_D + 56°$, and was shown to possess the formula $C_{18}H_{32}O_2$. Although isomeric with linolic acid, it combined with only two atomic proportions of bromine or iodine, and must, therefore, contain in its structure both a closed ring and an ethylenic linking.

In a subsequent communication, entitled "The Constitution of Chaulmoogric Acid, Part I" (Trans., 1904, **85**, 851), several derivatives of this new acid were described. It was also shown that, for an unsaturated compound, it exhibited certain remarkable properties, since it was unattacked by fused alkalis, even at 300°, and when boiled with sodium and amyl alcohol the ethylenic linking was not reduced.

When oxidised in alkaline solution with potassium permanganate, dihydroxydihydrochaulmoogric acid, $C_{18}H_{32}O_2(OH)_2$, was obtained, together with formic acid, and an acid possessing the formula

$$C_{15}H_{28}O(CO_2H)_2.*$$

The authors have extended the study of chaulmoogric acid, more especially with regard to the products furnished by its oxidation with potassium permanganate. The present communication embodies the results obtained, and the conclusions which may be drawn from them respecting the constitution of this acid.

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* An ester, to which the formula $C_{15}H_{28}(CO_2Et)_2$ was previously ascribed, has now been found to have consisted of impure ethyl dodecanedicarboxylate. No acid of the formula $C_{15}H_{28}(CO_2H)_2$ is produced by the oxidation of chaulmoogric acid.

When a dilute aqueous solution of chaulmoogric acid in an excess of potassium hydroxide is treated at temperatures below 10° with an amount of potassium permanganate equivalent to one atomic proportion of oxygen, a considerable portion of the acid is recovered unchanged. This is due to the very sparing solubility of the potassium salt in water at low temperatures. If, however, an amount of permanganate equivalent to 2—3 atomic proportions of oxygen is employed at a temperature of 18—20°, two isomeric dihydroxydihydrochaulmoogric acids having the formula $C_{18}H_{32}O_2(OH)_2$ can be isolated, whilst formic acid is also produced. The acid to which the name *α-dihydroxydihydrochaulmoogric acid* may be applied melts at 105°, and has $[\alpha]_D +11\cdot6°$. It is identical with the dihydroxy-acid previously described (Power and Gornall, *loc. cit.*). The isomeric acid, designated as *β-dihydroxydihydrochaulmoogric acid*, melts at 93°, and has $[\alpha]_D -14\cdot2°$.

On repeating the oxidation with the use of an amount of permanganate equivalent to four atomic proportions of oxygen, an acid of the formula $C_{18}H_{32}O_4$ was produced. This was isolated in the form of its methyl ester, which had the composition $C_{19}H_{34}O_4$, melted at 64°, and gave a semicarbazone melting at 110°. It thus appears that this is the methyl ester of a *hydroxyketodihydrochaulmoogric acid*. On hydrolysis with alcoholic sodium hydroxide this ester neutralised two equivalents of the alkali, notwithstanding the fact that it is derived from a monocarboxylic acid. This property is probably due to the opening of the ring by the hydrolysis of the grouping ·CH(OH)·CO·, with the formation of the sodium salt of a hydroxydicarboxylic acid,

$$C_{18}H_{34}O_5.$$

The acid liberated from this salt was found to have the formula

$$C_{18}H_{32}O_4,$$

but it did not again yield the original ester, and would therefore appear to be a lactonic acid, formed by the elimination of a molecule of water.

By the oxidation of chaulmoogric acid in alkaline solution with an excess of permanganate, an amount of the latter equivalent to 6—7 atomic proportions of oxygen was consumed. A *tricarboxylic acid* (m. p. 68°), having the formula $C_{18}H_{32}O_6$, was thus obtained, together with *n*-dodecanedicarboxylic acid, $[CH_2]_{12}(CO_2H)_2$, a smaller quantity of *n*-undecanedicarboxylic acid, $[CH_2]_{11}(CO_2H)_2$, and still smaller quantities of oxalic and malonic acids. The tricarboxylic acid is a very stable compound, and the numerous attempts to obtain from it such degradation products as would throw light on its constitution were unsuccessful.

In order to ascertain whether the same products would be obtained under different conditions, an oxidation of chaulmoogric acid was conducted in acetic acid solution. The *n*-dodecanedicarboxylic acid and the tricarboxylic acid, $C_{18}H_{32}O_6$, were again produced, and, in addition to these, a keto-dicarboxylic acid, $C_{17}H_{30}O_5$ (m. p. 128°), identical with the acid of this formula described in the previous communication (*loc. cit.*). When this keto-acid is oxidised in alkaline solution with an amount of potassium permanganate equivalent to three atomic proportions of oxygen, the principal product is *n*-dodecanedicarboxylic acid, which is apparently associated with a small quantity of *n*-undecanedicarboxylic acid. The constitution of this keto-acid may therefore be represented by the formula $CO_2H\cdot[CH_2]_2-\vdots-CO\cdot[CH_2]_{12}\cdot CO_2H$, oxidation taking place principally at the place indicated by the dotted line with the production of *n*-dodecanedicarboxylic and malonic acids, and also, to a much less extent, at the other side of the carbonyl group, yielding *n*-undecanedicarboxylic and succinic acids. The amount of succinic acid formed was not sufficient to permit of its identification, but malonic acid, as already stated, has been identified as a product of the oxidation of chaulmoogric acid with an excess of permanganate. The extreme ease with which this keto-acid is broken down by alkaline permanganate doubtless accounts for the fact that no appreciable amount of it could be isolated from the products afforded by the oxidation of chaulmoogric acid with this reagent.

By the addition of hydrogen bromide to ethyl chaulmoograte, *ethyl bromodihydrochaulmoograte* is formed, which is optically active, having $[\alpha]_D$ +3·88°. When the latter ester is reduced with zinc dust and acetic acid it gives *ethyl dihydrochaulmoograte*, $C_{17}H_{33}\cdot CO_2Et$ (m. p. 17°), which is optically inactive. It would therefore appear that the asymmetry of the chaulmoogric acid molecule is destroyed when the ethylenic linking is resolved by the addition of two atoms of hydrogen. When the elements of hydrogen bromide are split off from ethyl bromodihydrochaulmoograte the original ester is not regenerated, but a product is obtained which has a rotatory power of about +7°30′ in a 1-dcm. tube. The latter ester, on hydrolysis, afforded a mixture of acids, from which, on oxidation with permanganate, a *ketodicarboxylic acid*, $C_{18}H_{32}O_5$ (m. p. 126°), was obtained.

A consideration of the results recorded in this communication renders it evident that the constitution of chaulmoogric acid cannot be represented by any single formula. In the first place, by its limited oxidation, it yields two dihydroxy-acids, and, furthermore, when more completely oxidised, two series of products are obtained. These products are, on the one hand, a stable tricarboxylic acid, $C_{18}H_{32}O_6$, and, on the other, formic acid and a ketodicarboxylic acid,

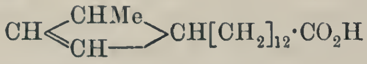
$$CO_2H\cdot[CH_2]_2\cdot CO\cdot[CH_2]_{12}\cdot CO_2H,$$

the latter, by further oxidation, yielding *n*-dodecane and *n*-undecanedicarboxylic acids.

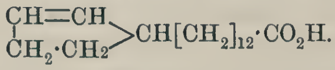
The formation of a tricarboxylic acid, $C_{18}H_{32}O_6$, possessing the same number of carbon atoms as chaulmoogric acid, shows that the ethylenic linking is contained in the ring, and not in an allylic grouping, as was previously supposed.

The carbon chain $\cdot[CH_2]_{12}\cdot CO_2H$ contained in the keto-acid must be present in the original chaulmoogric acid molecule, and it therefore follows that the ring contained in the latter can consist of not more than five carbon atoms.

As chaulmoogric acid, from the nature of its oxidation products, cannot be a trimethylene compound, it must contain either a methyl*cyclo*butene or a *cyclo*pentene ring. The formation of the tricarboxylic acid would then be explained by assigning to chaulmoogric acid one of the following formulæ:

(I)


$$\mathrm{CH}\left<\begin{matrix}\mathrm{CHMe}\\ \mathrm{CH}\text{——}\end{matrix}\right>\mathrm{CH[CH_2]_{12}\cdot CO_2H}$$

(II)


$$\left.\begin{matrix}\mathrm{CH{=}CH}\\ |\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right>\mathrm{CH[CH_2]_{12}\cdot CO_2H.}$$

The product formed by the addition of hydrogen bromide to ethyl chaulmoograte is, as stated above, optically active, but on reducing this product with zinc dust and acetic acid the resulting ethyl dihydrochaulmoograte is inactive. It is inconceivable, however, that racemisation could be effected by a simple process of reduction when it is not brought about by treatment with hydrogen bromide or even by distilling the resulting product. From these considerations it seems highly probable that dihydrochaulmoogric acid no longer contains an asymmetric carbon atom, whereas if derived from formula I it would contain two such carbon atoms. Moreover, the ketodicarboxylic acid, $C_{17}H_{30}O_5$, if derived from a methyl*cyclo*butene compound, would have the constitution $CO_2H\cdot CHMe\cdot CO[CH_2]_{12}\cdot CO_2H$, and would give on oxidation *n*-dodecanedicarboxylic and acetic acids, whereas it has been shown that malonic acid is formed and not acetic acid.

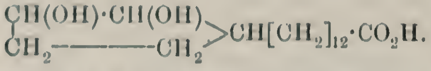
From these considerations it follows that formula II may correctly be assigned to chaulmoogric acid. The tricarboxylic acid,

$$C_{18}H_{32}O_6,$$

will therefore be *n-pentadecane-αα′γ-tricarboxylic acid*,

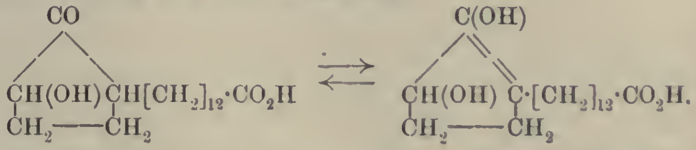
$$CO_2H\cdot[CH_2]_2\cdot CH\cdot(CO_2H)\cdot[CH_2]_{12}\cdot CO_2H,$$

and the constitution of the dihydroxydihydrochaulmoogric acid, which by its oxidation yields this tricarboxylic acid, may be represented by the formula:



$$\left.\begin{matrix}\mathrm{CH(OH)\cdot CH(OH)}\\ |\qquad\qquad\\ \mathrm{CH_2\text{————}CH_2}\end{matrix}\right>\mathrm{CH[CH_2]_{12}\cdot CO_2H.}$$

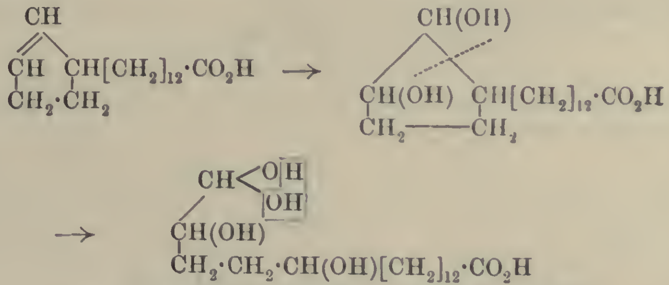
The tricarboxylic acid, although optically inactive, still contains an asymmetric carbon atom. The racemisation probably takes place in the hydroxyketo-acid, and may be attributed to keto-enolic tautomerism occurring in the following manner:



The optically inactive hydroxyketo-acid obtained is therefore probably represented by the above formula.

The formation of the ketodicarboxylic acid, $C_{17}H_{30}O_5$, remains to be considered. That it cannot have been formed by the further oxidation of the tricarboxylic acid is shown by the great stability of this compound towards alkaline permanganate solution. Moreover, as this keto-acid is the only acid obtained which possesses but one atom of carbon less than chaulmoogric acid, its formation is probably accompanied by the production of the formic acid which occurs amongst the products of oxidation.

The formation of these two acids from the formula deduced above for chaulmoogric acid could only be explained in the following manner:

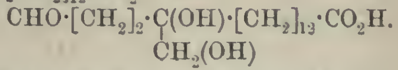


$$\longrightarrow \quad HCO_2H + CO_2H{\cdot}[CH_2]_2{\cdot}CO{\cdot}[CH_2]_{12}{\cdot}CO_2H.$$

Experience has shown, however, that in every instance of the oxidation of a compound possessing a ring containing a double linking, the ring opens at that point alone, so that this explanation must be considered improbable.

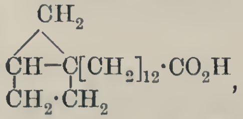
There are two hypothetical acids from which the above mentioned keto-acid and formic acid could have been formed by further oxidation, namely, those possessing the following formulæ:

(I) $CH_2(OH){\cdot}CH(OH){\cdot}[CH_2]_2{\cdot}CO{\cdot}[CH_2]_{12}{\cdot}CO_2H$ and

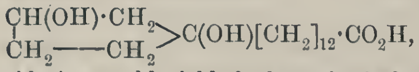
(II) 

$$CHO{\cdot}[CH_2]_2{\cdot}\underset{CH_2(OH)}{C}(OH){\cdot}[CH_2]_{13}{\cdot}CO_2H.$$

These two hypothetical acids could, however, not be produced from an acid of the formula deduced above for chaulmoogric acid. If, on the other hand, the constitution of chaulmoogric acid were to be represented by the formula:



it will be seen that the formation of these products can readily be explained. The second dihydroxydihydrochaulmoogric acid will then have the following structure,



and on further oxidation could yield the hypothetical compounds represented above, and, consequently, the ketodicarboxylic acid, $C_{17}H_{30}O_5$, and formic acid.

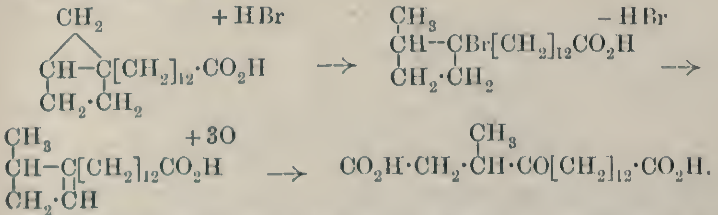
The ketodicarboxylic acid, $C_{18}H_{32}O_5$, obtained by the oxidation of the acids produced by removing the elements of hydrogen bromide from ethyl bromodihydrochaulmoograte, was at first thought to have been derived from the *cyclo*pentene structure deduced for chaulmoogric acid, and therefore to have the formula

$$CO_2H{\cdot}[CH_2]_3{\cdot}CO{\cdot}[CH_2]_{12}{\cdot}CO_2H,$$

which would give succinic acid on further oxidation. It was found, however, that, instead of succinic acid, oxalic, formic, and acetic acids were formed, and from these facts the formula

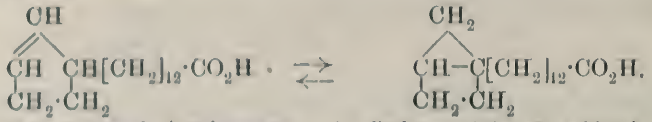
$$CO_2H{\cdot}CH_2{\cdot}CHMe{\cdot}CO[CH_2]_{12}{\cdot}CO_2H$$

may be deduced. This acid can be considered to have been formed by the following reactions:



Dihydrochaulmoogric acid may therefore be considered a mixture of *a-carboxy*-n-*dodecyl*cyclo*pentane* and 1-*a-carboxy*-n-*dodecyl*-2-*methyl*-cyclo*butane*.

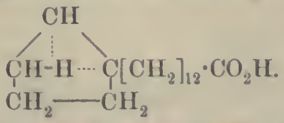
From the foregoing considerations it is seen that the behaviour of chaulmoogric acid can be explained by assigning to it both the following formulæ:



1-*a-Carboxy*-n-*dodecyl*-Δ⁴-cyclo*pentene*. 1-*a-Carboxy*-n-*dodecyl*-1 : 4-bicyclo*pentane*.

Chaulmoogric acid has, however, all the properties of an individual substance. It has, moreover, been obtained from the seeds of three botanically distinct species of plants, and in all cases it possesses identical properties. In addition to this, a homologue of it, hydnocarpic acid, $C_{16}H_{28}O_2$, has been isolated (Trans., 1905, **87**, 888), which shows an analogous behaviour on oxidation, and, like chaulmoogric acid, has all the characters of an individual substance. For these reasons it cannot be considered possible that chaulmoogric acid is a mixture of stable isomerides, and it must therefore be regarded as being in a state of tautomerism between the two formulæ represented above, or at all events existing in such a state as to undergo chemical change in accordance with both these formulæ.

This conclusion respecting the constitution of chaulmoogric acid may also be expressed by a formula analogous to that proposed by Thorpe for glutaconic acid (Trans., 1905, **87**, 1669) as follows:



$$\begin{array}{l} \qquad\;\; \mathrm{CH} \\ \quad\;\; \diagup \;\vdots\; \diagdown \\ \mathrm{CH{-}H \cdots C[CH_2]_{12}{\cdot}CO_2H.} \\ \mathrm{CH_2 \text{———} CH_2} \end{array}$$

In this formula the dotted lines represent a state of equilibrium between the hydrogen atom and two carbon atoms.

The results obtained by Sir W. H. Perkin for the molecular magnetic rotation of ethyl chaulmoograte, as previously recorded (Trans., 1904, **85**, 851), are quite in harmony with the above conclusion. The average value found at 14° (21·02) lies between that calculated for the ester if it possessed the pentene structure (21·31) and that for the bicyclic structure (19·51). Sir W. H. Perkin has now kindly determined the rotation of ethyl chaulmoograte at a higher temperature, when for a rise of 68·6° a diminution of 0·231 in the molecular magnetic rotation was observed, but as a small reduction with rise of temperature is usual amongst such compounds no deduction can be drawn from this observation.

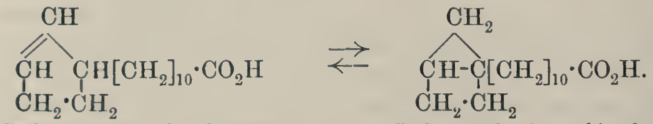
A determination of the molecular magnetic rotation of chaulmoogric acid at 84° gave a result analogous to that obtained for its ethyl ester, inasmuch as the value found (19·031) lies between the numbers calculated for the two formulæ suggested for this acid.

Hydnocarpic acid, $C_{16}H_{28}O_2$ (m. p. 60°; $[\alpha]_D + 68°$), the isolation of which has previously been described (Trans., 1905, **87**, 884), is a homologue of chaulmoogric acid, and is associated with the latter in the three fatty oils from which it has been obtained. The two acids are in every respect similar in their properties, and are evidently of closely analogous constitution.

From a consideration of the constitutional formulæ assigned to chaulmoogric acid it was to be expected that hydnocarpic acid would possess essentially the same structure, the only difference being in the length of the side chain. This proved to be the case, for, on oxidation in alkaline solution with an excess of potassium permanganate, hydnocarpic acid yielded *n*-decanedicarboxylic acid, $[CH_2]_{10}\cdot(CO_2H)_2$, and a tricarboxylic acid, $C_{16}H_{28}O_6$ (m. p. 60°), which is considered to be n-*tridecane-aa′γ-tricarboxylic acid*,

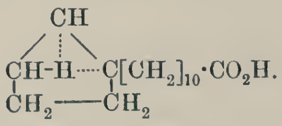
$$CO_2H\cdot[CH_2]_2\cdot CH(CO_2H)\cdot[CH_2]_{10}\cdot CO_2H.$$

The following formulæ may therefore be ascribed to hydnocarpic acid:



1-*a-Carboxy*-n-*decyl*-Δ^4-cyclo*pentene*. 1-*a-Carboxy*-n-*decyl*-1 : 4-bicyclo*pentane*.

These may be expressed, as in the case of chaulmoogric acid, by one formula, as follows:



EXPERIMENTAL.

I. *Chaulmoogric Acid*, $C_{18}H_{32}O_2$.

The chaulmoogric acid employed in this investigation was prepared from genuine chaulmoogra oil (from the seeds of *Taraktogenos Kurzii*, King). The oil was hydrolysed with alcoholic potash, the acids liberated, fractionally crystallised from alcohol, and the chaulmoogric acid finally purified by distillation under diminished pressure and recrystallisation from alcohol (compare Trans., 1904, **85**, 846). It was then obtained in colourless, glistening leaflets, and, when freshly distilled, melted at 68·5°, and had $[a]_D$ + 62·1° in chloroform solution. After keeping for some time the optical rotatory power of the acid becomes somewhat diminished and it acquires a slightly yellow colour. If it be then again distilled, a dark brown substance is left in the distilling flask, which is probably formed by polymerisation.

Oxidation of Chaulmoogric Acid in Alkaline Solution with Potassium Permanganate (O = 2—3 *Atomic Equivalents*).—One hundred grams of chaulmoogric acid were dissolved in a solution of 50 grams of potassium hydroxide in 5 litres of water, and to this were added 5 litres of a 2 per cent. solution of permanganate, the temperature being kept between 16° and 20°. The whole of the permanganate was instantly reduced. After filtering, the liquid was made nearly neutral with sulphuric acid, and concentrated to a small bulk. The acids were then liberated, and steam passed through the liquid in order to remove any volatile acid. The distillate was found to contain a small amount of formic acid, which was identified by the usual tests and by the analysis of its barium salt:

0·3002 gave 0·3060 $BaSO_4$. Ba = 60·0.

$(CO_2H)_2Ba$ requires Ba = 60·4 per cent.

This acid was evidently produced by the further oxidation of one of the dihydroxydihydrochaulmoogric acids subsequently described.

The non-volatile acids remaining in the distilling flask were extracted, and converted into their methyl esters by treatment with methyl alcohol and sulphuric acid. The product was then distilled under a pressure of 16 mm., when the following fractions were collected: 200—220°; 220—245°; 245—260°; 260—275°; 275—290°/16 mm There then remained in the flask a quantity (22 grams) of an undistillable oil, which apparently consisted of condensation products.

Fraction 200—220°/16 mm.—This was analysed with the following result:

0·1030 gave 0·2519 CO_2 and 0·0964 H_2O. C = 66·7; H = 10·4.

$C_{16}H_{30}O_4$ requires C = 67·1; H = 10·5 per cent.

It evidently consisted chiefly of the methyl ester of *n*-dodecanedicarboxylic acid, $C_{16}H_{30}O_4$, which was obtained in larger quantity by the oxidation of chaulmoogric acid with an excess of permanganate, and its identity established.

Fractions 220—245° *and* 245—260°/16 mm.—These were small in amount, and were found to consist of mixtures of the constituents of the fractions of lower and higher boiling point.

Isolation of Two Dihydroxydihydrochaulmoogric Acids, $C_{17}H_{31}(OH)_2\cdot CO_2H$.

Fraction 260—275°/16 mm.—This was the largest fraction obtained. On cooling, it deposited a considerable quantity of a solid substance, which was brought on a porous plate to remove adhering oil, after which it melted at 60—68°:

0·0933 gave 0·2366 CO_2 and 0·0910 H_2O. C = 69·2; H = 10·8.

$C_{19}H_{36}O_4$ requires C = 69·5; H = 11·0 per cent.

This substance agreed in composition with a methyl ester of dihydroxydihydrochaulmoogric acid. After several crystallisations from methyl alcohol it yielded an ester crystallising in long, glistening needles, which melted at 75—76°, and this melting point was not changed by further crystallisation:

0·1056 gave 0·2669 CO_2 and 0·1045 H_2O. C = 68·9; H = 11·0.

$C_{17}H_{31}(OH)_2\cdot CO_2Me$ requires C = 69·5; H = 11·0 per cent.

0·3360 gram in 100 c.c. of chloroform gave α_D +0°5′ in a 2-dcm. tube, whence $[\alpha]_D$ +12·4°.

The ester was hydrolysed and the acid extracted and crystallised from ethyl acetate, in which it was readily soluble. It separated in clusters of small, silky needles, melting at 105°:

0·0944 gave 0·2368 CO_2 and 0·0922 H_2O. C = 68·4; H = 10·8.

$C_{18}H_{34}O_4$ requires C = 68·8; H = 10·8 per cent.

0·5008 gram in 100 c.c. of absolute alcohol gave α_D +0°7′ in a 2-dcm. tube, whence $[\alpha]_D$ +11·6°.

This acid is thus shown to be a dihydroxydihydrochaulmoogric acid, and was found to be identical with the acid of the same composition described in the previous communication, the melting point of which was given as 102° (Trans., 1904, **85**, 860).

The mother liquors from the crystallisation of the ester melting at 75—76° were found to be lævorotatory, and from them an ester was isolated which, after several crystallisations, melted at 68—69°. This ester crystallised in silky needles, and was much more soluble in methyl alcohol than the one of higher melting point which was previously isolated:

0·8420 gram in 100 c.c. of chloroform gave α_D −0°16′ in a 2-dcm. tube, whence $[\alpha]_D$ −15·8°.

On hydrolysing this ester an acid was obtained which, after two crystallisations from ethyl acetate, melted at 92—93°:

0·1004 gave 0·2520 CO_2 and 0·0986 H_2O. C = 68·5; H = 10·9.

$C_{18}H_{32}O_2(OH)_2$ requires C = 68·8; H = 10·8 per cent.

0·2936 gram in 25 c.c. of absolute alcohol gave α_D −0°20′ in a 2-dcm. tube, whence $[\alpha]_D$ −14·2°.

This acid is therefore an isomeride of that melting at 105°, but it is much more sparingly soluble in ethyl acetate than the latter. Both these acids yield sodium salts which are only sparingly soluble in cold water.

Fraction 275—290°/16 mm.—This evidently also contained some of the two dihydroxydihydrochaulmoogric acids which were isolated from the preceding fraction.

Oxidation of Chaulmoogric Acid in Alkaline Solution with Potassium Permanganate (O = 4 *Atomic Equivalents*).—One hundred grams of chaulmoogric acid were dissolved in the same amount of solution of potassium hydroxide as in the preceding experiment, and to this was added a solution of 150 grams of potassium permanganate in 8 litres of water, the temperature of the mixture being kept at 15—18°. The acids were extracted, converted into their methyl esters, and fractionally distilled under a pressure of 15 mm. Several fractions were collected, of which those boiling at 265—275° and 275—285°/15 mm. solidified on cooling.

Isolation of a Hydroxyketodihydrochaulmoogric Acid, $C_{17}H_{30}O(OH)\cdot CO_2H$.

Fraction 265—275°/15 mm.—This was the larger of the two fractions, and on analysis it gave the following result:

0·0961 gave 0·2410 CO_2 and 0·0882 H_2O. C = 68·4; H = 10·2 per cent.

After being brought on a porous plate to remove adhering oil, the solid ester was crystallised several times from methyl alcohol, when it separated in needles melting at 64°, and this melting point was not altered by further crystallisation:

0·1051 gave 0·2697 CO_2 and 0·0986 H_2O. C = 70·0; H = 10·4.
0·1003 ,, 0·2577 CO_2 ,, 0·0940 H_2O. C = 70·1; H = 10·4.
$C_{19}H_{34}O_4$ requires C = 69·9; H = 10·4 per cent.

The solid which separated from the fraction 275—285°/15 mm. likewise consisted of the above-described ester.

The ester was hydrolysed, and the acid extracted and crystallised from alcohol, from which it separated in needles melting at 90°. It was very soluble in cold ethyl acetate, but less freely in alcohol:

0·1162 gave 0·2946 CO_2 and 0·1060 H_2O. C = 69·1; H = 10·1.
0·1013 ,, 0·2573 CO_2 ,, 0·0920 H_2O. C = 69·3; H = 10·1.
0·0984 ,, 0·2477 CO_2 ,, 0·0913 H_2O. C = 68·8; H = 10·3.
$C_{18}H_{32}O_4$ requires C = 69·2; H = 10·3 per cent.
$C_{17}H_{30}O_4$,, C = 68·4; H = 10·1 ,,

From these results it is evident that the acid has the formula $C_{18}H_{32}O_4$. Both acid and ester were optically inactive.

The methyl ester, when treated with semicarbazide hydrochloride and sodium acetate, yielded a semicarbazone which crystallised from alcohol in small needles melting at 110°. This shows the ester to be that of a hydroxyketodihydrochaulmoogric acid.

0·5108 of the ester required for hydrolysis 6·4 c.c. $N/2$ NaOH, the calculated amount for $C_{16}H_{29}O_2(CO_2Me)$ being 3·1 c.c.

The fact that this substance, although the ester of a monocarboxylic acid, when heated with an excess of alkali neutralises two equivalents of the latter, is probably due to hydrolysis of the grouping $\cdot CH(OH)\cdot CO\cdot$ in the ring, with the formation of a dibasic hydroxy-acid, $C_{18}H_{34}O_5$, and the latter then apparently loses water, yielding a lactonic acid, $C_{18}H_{32}O_4$. This assumption receives support from the fact that no semicarbazone could be obtained from the acid furnished by the hydrolysis of the ester, and, on re-esterifying the acid, instead of the original ester, a fatty substance was obtained. The amount of material available was insufficient for its further investigation.

Oxidation of Chaulmoogric Acid in Alkaline Solution with an Excess of Potassium Permanganate.—One hundred grams of chaulmoogric acid were dissolved in an aqueous solution of 50 grams of potassium hydroxide, and the opalescent liquid diluted with water to the measure of 5 litres. This was allowed to flow slowly, with constant stirring, into 11 litres of a 3 per cent. solution of potassium permanganate, the temperature being kept below 20° by the addition of ice. After standing for some hours, the excess of permanganate was removed by sodium bisulphite. The liquid was then heated, filtered, the filtrate concentrated, acidified with sulphuric acid, and distilled with steam. The distillate contained an acid which was converted into its barium salt, and from this a silver salt was prepared and analysed:

0·3024 gave 0·1960 Ag. Ag = 64·8.

$C_2H_3O_2Ag$ requires Ag = 64·7 per cent.

The volatile product was thus identified as acetic acid. From the results of an experiment subsequently described, this appears to have been produced by the decomposition of malonic acid, and not to have been a direct product of oxidation.

The non-volatile acids were then extracted and converted into their methyl esters. On distilling the product under 15 mm. pressure the following fractions were obtained: below 220° (45 grams); 220—260° (8 grams); 260—270° (55 grams); 270—280°/15 mm. (5 grams). These fractions were all optically inactive, and were subsequently examined as follows.

Isolation of n-*Undecane and* n-*Dodecane Dicarboxylic Acids.*

Fraction boiling below 220°/15 mm.—This was fractionally distilled under 15 mm. pressure, when it was further resolved into the following fractions: (*a*) below 200° (5 grams); (*b*) 200—205 (13 grams); (*c*) 205—210° (3 grams); (*d*) 210—215°/15 mm. (13 grams).

Fraction (*c*) and (*d*), on standing, deposited a crystalline substance, which was collected and crystallised from methyl alcohol. It then separated in clusters of needles melting at 41°:

0·1335 gave 0·3272 CO_2 and 0·1256 H_2O. C = 66·8; H = 10·5.
0·1279 ,, 0·3132 CO_2 ,, 0·1204 H_2O. C = 66·8; H = 10·5.

$C_{16}H_{30}O_4$ requires C = 67·1; H = 10·5 per cent.

0 6876 required for hydrolysis 9·5 c.c. *N*/2 NaOH, the calculated amount for $C_{12}H_{24}(CO_2Me)_2$ being 9·6 c.c.

By the hydrolysis of this ester an acid somewhat sparingly soluble in ether was obtained. It was crystallised from ethyl acetate, from which it separated in small, glistening leaflets melting sharply at 124°:

0·0935 gave 0·2234 CO_2 and 0·0859 H_2O. C = 65·2 ; H = 10·2.
0·1208 „ 0·2879 CO_2 and 0·1098 H_2O. C = 65·0 ; H = 10·1.
$C_{14}H_{26}O_4$ requires C = 65·1 ; H = 10·1 per cent.

This substance agrees in composition and melting point with *n*-dodecanedicarboxylic acid, $[CH_2]_{12}(CO_2H)_2$, obtained by Brown and Walker by the electrolysis of potassium ethyl suberate (*Annalen*, 1891, **261**, 123). In order to confirm its identity with the above-mentioned acid, its diethyl ester was prepared. This was found to have the same melting point (28°) as a specimen of the synthetic ester which was kindly supplied to us by Professor A. Crum Brown, and a mixture of the two esters showed no diminution in melting point. A mixture of the two acids likewise melted at the same temperature (124°) at which each separately fused.

The fraction (*b*), b. p. 200—205°/15 mm., deposited no solid ester, even on long standing. It was therefore hydrolysed and the acids extracted. These melted indefinitely at 93—105°, but after several crystallisations from ethyl acetate an acid was obtained which separated in small, glistening needles, melting at 112°, and this melting point was not changed by further crystallisation :

0·1093 gave 0·2553 CO_2 and 0·0956 H_2O. C = 63·7 ; H = 9·7.
0·1158 „ 0·2700 CO_2 „ 0·1029 H_2O. C = 63·6 ; H = 9·9.
$C_{13}H_{24}O_4$ requires C = 63·9 ; H = 9·8 per cent.

This substance agrees in composition and melting point with the brassylic acid, $C_{13}H_{24}O_4$ [regarded as *n*-undecanedicarboxylic acid, $[CH_2]_{11}(CO_2H)_2$], obtained by Grossmann by the oxidation of behenolic acid, and is undoubtedly identical with it (*Ber.*, 1893, **26**, 645).

From the fraction of esters (*a*), boiling below 200°/15 mm., of which after several oxidations further quantities were accumulated, adipic, *n*-pimelic, and suberic acids were isolated, whilst higher members of the same series were also found to be present. It was ascertained, however, by some other experiments that these acids were produced by the long continued action of permanganate on the above-mentioned *n*-undecane- and *n*-dodecane-dicarboxylic acids.

Fraction 220—260°/15 mm.—This was small in amount (8 grams), and consisted of a mixture of the constituents of the fraction boiling below 220°/15 mm. and those of the fraction of higher boiling point.

Isolation of a Tricarboxylic Acid, $C_{18}H_{32}O_6$ (n-*Pentadecane-aa′γ-tricarboxylic Acid*).

Fraction 260—270°/15 mm.—This fraction, which was the largest obtained, crystallised and became almost completely solid on standing. It was drained on a porous plate, to remove a small quantity of adhering oil, and then dissolved in warm methyl alcohol, from which, on cooling, it separated in beautiful clusters of needles, melting at 38·5°. On further crystallisation the melting point remained unchanged. It distilled at 260°/15 mm.:

0·1355 gave 0·3232 CO_2 and 0·1204 H_2O. C = 65·0; H = 9·9.
0·1278 „ 0·3046 CO_2 „ 0·1153 H_2O. C = 65·0; H = 10·0.
0·1064 „ 0·2542 CO_2 „ 0·0936 H_2O. C = 65·1; H = 9·8.
$C_{14}H_{26}O_4$ requires C = 65·1; H = 10·1 per cent.
$C_{17}H_{30}O_5$ „ C = 65·0; H = 9·6 „
$C_{21}H_{38}O_6$ „ C = 65·3; H = 9·8 „

2·3979 required for hydrolysis 36·4 c.c. *N*/2 NaOH. The calculated amount for both $C_{10}H_{20}(CO_2Me)_2$ and $C_{15}H_{29}(CO_2Me)_3$ is 37·2 c.c., whereas $C_{13}H_{24}O(CO_2Me)_2$ would require only 30·5 c.c.

The ester was hydrolysed and the acid extracted with ether. After removing the solvent an oil was obtained which solidified to an amorphous, fatty looking mass, melting at 61—63°; and difficulty was experienced in obtaining it crystalline. When, however, a portion was kept at 62° for some time it slowly solidified, and was seen to consist of small, slender needles. The main portion was then dissolved in an equal quantity of ethyl acetate, and the solution inoculated with the above-mentioned crystals, when the acid separated in hard aggregates of microscopic needles, which melted sharply at 68°. It was optically inactive:

0·1086 gave 0·2501 CO_2 and 0·0912 H_2O. C = 62·8; H = 9·3.
0·1144 „ 0·2630 CO_2 „ 0·0967 H_2O. C = 62·7; H = 9·4.
0·1229 „ 0·2816 CO_2 „ 0·1032 H_2O. C = 62·5; H = 9·3.
$C_{12}H_{22}O_4$ requires C = 62·6; H = 9·6 per cent.
$C_{18}H_{32}O_6$ „ C = 62·8; H = 9·3 „

Of these two formulæ the second seemed improbable, on account of the inference previously drawn from the magnetic rotation of chaulmoogric acid that it possessed an allylic grouping (Trans., 1904, 85, 855). On the other hand, the boiling point of the ester was much higher than would be expected had the acid the formula $C_{12}H_{22}O_4$. In order, therefore, to decide respecting the formula of the acid, molecular weight determinations were made of it and of its methyl and ethyl esters, and the propyl ester was also prepared and analysed:

0·9756 of the acid in 100 phenol gave Δt – 0·21°. M.W. = 343.
0·9902 „ „ 100 benzene „ Δt – 0·15°. M.W. = 323.
$C_{18}H_{32}O_6$ requires M.W. = 344.

Methyl Ester.—3·283 in 100 benzene gave Δt - 0·41°. M.W- = 392.
$C_{14}H_{26}O_4$ = 258; $C_{21}H_{38}O_6$ = 386.

Ethyl Ester.—This was obtained as a colourless oil, which distilled at 275°/15 mm.:

0·1151 gave 0·2835 CO_2 and 0·1065 H_2O. C = 67·2; H = 10·3.
0·0955 ,, 0·2358 CO_2 ,, 0·0886 H_2O. C = 67·3; H = 10·3.
1·3341 in 100 benzene gave $\Delta t - 0\cdot15°$. M.W. = 436.
$C_{16}H_{30}O_4$ requires C = 67·1; H = 10·5 per cent. M.W. = 286.
$C_{24}H_{44}O_6$,, C = 67·3; H = 10·3 ,, M.W. = 428.

Propyl Ester.—This was obtained as a viscid, colourless oil, which boiled at 302°/24 mm.:

0·1159 gave 0·2916 CO_2 and 0·1108 H_2O. C = 68·6; H = 10·6.
0·1331 ,, 0·3360 CO_2 ,, 0·1278 H_2O. C = 68·8; H = 10·7.
$C_{18}H_{34}O_4$ requires C = 68·8; H = 10·8 per cent.
$C_{27}H_{50}O_6$,, C = 68·9; H = 10·6 ,,

From these results it is evident that the fraction boiling at 260—270°/15 mm. consists essentially of the trimethyl ester of a tricarboxylic acid having the formula $C_{18}H_{32}O_6$, and, from considerations which are discussed in the introductory portion of this paper, it is seen that this acid is n-*pentadecane-αα′γ-tricarboxylic acid.*

n-Pentadecane-*αα′γ*-tricarboxylic acid is very soluble in alcohol, ether, chloroform, or ethyl acetate, moderately so in benzene, and insoluble in water. It is an exceedingly stable substance. When heated with concentrated nitric acid it dissolved, but separated unchanged on cooling. When warmed with an alkaline solution of permanganate it was only very slowly attacked at temperatures below 70°. When, however, it was treated at this temperature with an excess of permanganate, it yielded succinic acid. Attempts were made to obtain a hydroxy-acid or lactone by oxidising with limited quantities of permanganate, but most of the acid was recovered unchanged. It is unattacked by a chromic acid mixture, a fact which is probably due to the insolubility of the organic acid in water. When treated with chromic acid in acetic acid solution, the greater portion was recovered unchanged, and no other definite product could be isolated. An attempt was also made to obtain from the acid an unsaturated compound. For this purpose it was brominated by the Volhard method, and the elements of hydrogen bromide subsequently eliminated, but the results were of a negative character.

Fraction 270—280°/15 mm.—This was small in amount, and consisted to a large extent of the ester of the above-mentioned tricarboxylic acid.

For the more complete examination of the lower acids formed by the oxidation of chaulmoogric acid, another portion was treated in alkali solution with permanganate, as previously described. After removing the excess of permanganate, and filtering, the liquid was made neutral with sulphuric acid and evaporated to dryness. The mixture of potassium salts thus obtained was powdered, thoroughly dried, suspended in absolute alcohol, and the acids esterified by passing dry hydrogen chloride through the boiling liquid for four hours. The mixture was then poured into water, the esters extracted with ether, and the ethereal solution washed with sodium carbonate and dried over sodium sulphate. After removing the ether, a quantity of alcohol distilled over, and, as this would contain the ester of any acetic acid produced by the oxidation, solid potash was added to it and the alcohol removed. The residue was then dissolved in water, the liquid acidified with sulphuric acid, and distilled with steam, but the distillate contained no acid. The ethyl esters, obtained as above described, were distilled under 30 mm. pressure, and the fraction boiling below 190°/30 mm., which was small in amount, fractionated under the ordinary pressure. Fractions were collected at 180—190°; 190—200; 200—210°, and 210—220°.

Fraction 180—190°.—A portion of this was shaken with concentrated aqueous ammonia, when an amide was formed which, when heated, decomposed without melting. The remainder of the fraction was hydrolysed in order to obtain the acid, which was identified as oxalic acid by its melting point and that of its methyl ester.

Fraction 190—200°.—This was analysed with the following result:

0·1213 gave 0·2321 CO_2 and 0·0808 H_2O. $C = 52{\cdot}2$; $H = 7{\cdot}4$.

$CH_2(CO_2Et)_2$ requires $C = 52{\cdot}5$; $H = 7{\cdot}5$ per cent.

By the hydrolysis of this ester an acid was obtained which melted somewhat indefinitely at 124—129° with effervescence, and, when more strongly heated, developed a distinct odour of acetic acid. This product of oxidation was therefore identified as malonic acid, and is, without doubt, the source of the acetic acid previously obtained.

Fractions 200—210° *and* 210—220°.—These were small in amount. The latter fraction was examined for the presence of succinic acid, but with a negative result.

Oxidation of Chaulmoogric Acid in Acetic Acid Solution with Potassium Permanganate.—To a solution of potassium permanganate (200 grams) in 90 per cent. acetic acid (1500 c.c.) was added an acetic acid solution of chaulmoogric acid (50 grams), the temperature being kept below 25°. After standing for some hours, the excess of permanganate and the manganese dioxide were reduced with sulphur dioxide, the white precipitate of manganese salts removed by filtration, and the filtrate evaporated under slightly reduced pressure. The salts thus obtained were then decomposed with sulphuric acid, and the acids extracted and converted into their methyl esters. On distilling these under 15 mm. pressure the following fractions were obtained:

200—220°; 220—255°; 255—260°; 260—270°/15 mm. The first, third, and fourth of these fractions solidified on standing.

Fraction 200—220°/15 mm.—On analysis this gave the following result:

0·1301 gave 0·3185 CO_2 and 0·1223 H_2O. C = 66·8; H = 10·5.

$C_{16}H_{30}O_4$ requires C = 67·1; H = 10·5 per cent.

This fraction evidently consisted of methyl *n*-dodecanedicarboxylate.

Fraction 220—255°/15 mm.—This was small in amount, and consisted of a mixture of the constituents of the preceding and succeeding fractions.

Isolation of a Ketodicarboxylic acid, $C_{17}H_{30}O_5$ (*γ-Keto-*n*-penta-decane-αα′-dicarboxylic Acid*).

Fraction 255—260° mm.—The crystalline solid which separated from this fraction was recrystallised from methyl alcohol, and was thus obtained in handsome plates, which melted sharply at 66°. On analysis:

0·1202 gave 0·2930 CO_2 and 0·1074 H_2O. C = 66·5; H = 9·9.

$C_{15}H_{28}O(CO_2Me)_2$ requires C = 66·7; H = 9·9 per cent.

By the hydrolysis of this ester an acid was obtained which was very sparingly soluble in ether. It was dried and crystallised from ethyl acetate, from which it separated in clusters of needles, melting at 128°. This acid was found to be identical with that of the same formula, $C_{17}H_{30}O_5$, and melting point described in the previous communication (Trans., 1904, **85**, 861). That it is a ketonic acid is shown by the following experiment.

One gram of the acid was dissolved in a dilute solution of potassium hydroxide, and to this was added a solution of 0·8 gram of hydroxylamine hydrochloride. The mixture was warmed for ten minutes, allowed to stand overnight, and then slightly acidified with sulphuric acid, when a substance separated which was soluble in an excess of acid. This was extracted with ether and crystallised from ethyl acetate, when it separated in small needles, melting at 83—84°:

0·1076 gave 0·2444 CO_2 and 0·0920 H_2O. C = 61·9; H = 9·5.

$C_{17}H_{31}O_5N$ requires C = 62·0; H = 9·4 per cent.

Oxidation of the Ketonic Acid, $C_{14}H_{28}CO(CO_2H)_2$.—This acid was found to be very stable towards permanganate in the absence of alkali, but to undergo oxidation readily in alkaline solution.

About 6 grams of the acid were dissolved in an aqueous solution of potassium hydroxide (5 grams), and mixed with an amount of permanganate solution equivalent to three atomic proportions of oxygen

(6 grams $KMnO_4$). Oxidation rapidly ensued with the development of heat, all the permanganate added being reduced. The acids were then extracted, converted into their methyl esters, and the latter distilled, when practically all passed over between 200 and 210°/15 mm. This fraction was analysed:

0·1396 gave 0·3394 CO_2 and 0·1316 H_2O. C = 66·3; H = 10·5.
$C_{15}H_{28}O_4$ requires C = 66·2; H = 10·3 per cent.
$C_{16}H_{30}O_4$ „ C = 67·1; H = 10·5 „

On standing, this fraction deposited a solid ester, which was collected and hydrolysed. The acid thus obtained, after several crystallisations, melted at 124°, and was identical with *n*-dodecanedicarboxylic acid, $[CH_2]_{12}(CO_2H)_2$, which had previously been separated from the products of the direct oxidation of chaulmoogric acid. It was evident, however, from the analysis of the above fraction, that it also contained the ester of *n*-undecanedicarboxylic acid.

Fraction 260—270°/15 mm.—This was spread on a porous plate to remove a little adhering oil, and then crystallised from methyl alcohol. A further quantity of the ester of the ketonic acid, melting at 66°, was separated from it, but the greater portion melted at 38°, and this was analysed:

0·1167 gave 0·2790 CO_2 and 0·1033 H_2O. C = 65·2; H = 9·8.
$C_{21}H_{38}O_6$ requires C = 65·3; H = 9·8 per cent.

This ester thus agreed in composition and melting point with the methyl *n*-pentadecane-$\alpha\alpha'\gamma$-tricarboxylate previously obtained, and a mixture of the two showed no diminution in melting point.

Action of Hydrogen Bromide on Ethyl Chaulmoograte.

One hundred grams of ethyl chaulmoograte were dissolved in 500 c.c. of light petroleum (b. p. 40—50°), and the solution, kept cool by means of ice, was saturated with dry hydrogen bromide. After remaining overnight, the solvent was removed by aspirating a current of dry air through the liquid under diminished pressure. The *ethyl bromodihydrochaulmoograte* thus obtained was a heavy, pale yellow liquid, having an agreeable odour. In moist air it slowly decomposed, evolving hydrogen bromide and becoming black. For the purpose of analysis a portion was repeatedly exposed to a gentle heat, and then placed in a vacuum desiccator containing paraffin wax and caustic potash.

0·1047 gave 0·2367 CO_2 and 0·0892 H_2O. C = 61·7; H = 9·5.
$C_{20}H_{37}O_2Br$ requires C = 61·7; H = 9·5 per cent.
$d\,20°/20° = 1·0778$.

2·8994 grams in 25 c.c. of chloroform gave α_D +0°54′ in a 2-dcm. tube, whence $[\alpha]_D$ +3·88°.

The same optical value was obtained from several different preparations, and it was not altered by their further treatment with hydrogen bromide.

Reduction of Ethyl Bromodihydrochaulmoograte.—A more convenient way of preparing dihydrochaulmoogric acid than that described in the previous communication (Trans., 1904, **85**, 857) has been found to be by the reduction of ethyl bromodihydrochaulmoograte with zinc dust and acetic acid. The *ethyl dihydrochaulmoograte* thus obtained distils at 230°/22 mm. When cooled, it solidifies to a mass of glistening needles, which melt at 17°. The dihydrochaulmoogric acid obtained by the hydrolysis of this ester melted at 71°, and is, as stated in the previous communication (*loc. cit.*), optically inactive. It is a very stable substance, and all attempts to prepare definite oxidation products from it resulted in its complete degradation.

Elimination of Hydrogen Bromide from Ethyl Bromodihydrochaulmoograte.—The bromo-ester was heated with an alcoholic solution of potassium hydroxide, when the elements of hydrogen bromide were eliminated with the simultaneous hydrolysis of the ester. The acid thus obtained was converted into the ethyl ester and the latter distilled. This had an optical rotation of +7°35′ in a 1-dcm. tube. When the hydrogen bromide was eliminated, either by the distillation of the bromo-ester or by heating it with diethylaniline, products were obtained which had a rotatory power respectively of +7°40′ and +7°20′ in a 1-dcm. tube.

The acid obtained by the action of alcoholic potash on the bromo-ester, as above described, when fractionally crystallised was found to be a mixture, and no pure substance could be isolated from it.

Formation of a Keto-dicarboxylic Acid, $C_{15}H_{30}CO(CO_2H)_2$.—The above mixture of acids was treated in the cold with an excess of potassium permanganate in the presence of only a slight excess of alkali. The acids thus produced were converted into their methyl esters, and the latter fractionally distilled under 15 mm. pressure. A portion boiling between 220 and 275°/15 mm. deposited a considerable quantity of a crystalline substance. This was collected and crystallised from methyl alcohol, from which it separated in beautiful plates, melting at 64—65°. On analysis:

0·0966 gave 0·2389 CO_2 and 0·0877 H_2O. C = 67·4; H = 10·1.
$C_{20}H_{36}O_5$ requires C = 67·4; H = 10·1 per cent.

This ester, on hydrolysis, yielded an acid which was almost insoluble in ether. The acid was collected, dried, and dissolved in hot ethyl acetate, from which, on cooling, it separated in small needles melting at 126°:

0·1128 gave 0·2716 CO_2 and 0·0988 H_2O. C = 65·7; H = 9·7.
$C_{18}H_{32}O_5$ requires C = 65·9; H = 9·8 per cent.

This was found to be a keto-acid, since it gave an *oxime* which, after crystallisation from ethyl acetate, melted at 67—68°.

Two-and-a-half grams of the acid were oxidised in alkaline solution with 3·8 grams of potassium permanganate. After removing the manganese dioxide, the liquid was concentrated, acidified with sulphuric acid, and distilled with steam. From the small amount of acid contained in the distillate a barium salt was prepared, which gave the reactions of formic and acetic acids.

The contents of the distillation flask were then diluted with water, and the insoluble acid separated by filtration. This was found to consist chiefly of *n*-dodecanedicarboxylic acid, which had previously been obtained by the direct oxidation of chaulmoogric acid. The filtrate was concentrated and extracted several times with ether, the ethereal solution dried with sodium sulphate, and the solvent removed, when a small quantity of a crystalline acid was obtained. This melted indefinitely between 100° and 130°, evolved gas at 150—160°, indicating the presence of some malonic acid, and at the latter temperature a substance sublimed in thin needles, which was identified as oxalic acid.

From considerations discussed in the introductory portion of the paper, it is seen that the above-described acid, $C_{18}H_{32}O_5$, is probably *γ-keto-β-methyl-*n*-pentadecane-αα′-dicarboxylic acid.*

II. *Hydnocarpic Acid*, $C_{16}H_{28}O_2$.

The hydnocarpic acid employed in this investigation was prepared from the oil of *Hydnocarpus Wightiana* (Blume) in the manner described by us in a previous communication (Trans., 1905, **87**, 888). It crystallises in colourless, glistening leaflets, melting at 60°, and having $[\alpha]_D$ + 68° in chloroform solution. Like its higher homologue, chaulmoogric acid, it undergoes change on keeping, acquiring a yellow colour, which is attended with a lowering of the melting point. If it be then distilled under diminished pressure, a brown, resinous substance is left in the distilling flask. This change takes place more readily with hydnocarpic than with chaulmoogric acid.

Oxidation of Hydnocarpic Acid in Alkaline Solution with an Excess of Potassium Permanganate.—Sixty-five grams of hydnocarpic acid were dissolved in a solution of 18 grams of potassium hydroxide in 3 litres of water. To this was gradually added, with constant stirring, a solution of 270 grams of potassium permanganate in 7 litres of water, the temperature during the oxidation being kept at 15—20°. After standing overnight, the excess of permanganate was removed with sodium bisulphite, and the liquid filtered. The acids were then liberated, extracted, and converted into their methyl esters. On distilling the latter under 18 mm. pressure the following fractions were obtained: 195—210°; 210—240°; 240—250°; 250—255°/18 mm. The first, third, and fourth of these fractions solidified almost completely on standing.

Isolation of n-*Decanedicarboxylic Acid.*

Fraction 195—210°/18 mm.—This was analysed with the following result:

0·1334 gave 0·3142 CO_2 and 0·1187 H_2O. C = 64·2; H = 9·9.
$C_{14}H_{26}O_4$ requires C = 65·1; H = 10·1 per cent.
$C_{13}H_{24}O_4$ „ C = 63·9; H = 9·8 „ „

This ester was hydrolysed and the acids crystallised from ethyl acetate. An acid was thus obtained which crystallised in small needles, melting at 123°:

0·1020 gave 0·2345 CO_2 and 0·0887 H_2O. C = 62·7; H = 9·7.
$C_{12}H_{22}O_4$ requires C = 62·6; H = 9·6 per cent.

This acid is evidently identical with the *n*-decamethylenedicarboxylic acid prepared synthetically by Nördlinger (*Ber.*, 1890, **23**, 2357), who found it to melt at 124·5—125·5°.

Fraction 210—240°/18 mm.—This was very small in amount, and consisted of the constituents of the preceding and succeeding fractions.

Isolation of a Tricarboxylic Acid, $C_{16}H_{28}O_6$ (n-*Tridecane-aa'γ-tricarboxylic Acid*).

Fractions 240—250° *and* 250—255°/18 mm.—The former of these two fractions was the largest obtained, but they were found to consist essentially of the same substance. The solid which separated from them was spread on a porous plate, in order to remove a little adhering oil, and then twice crystallised from methyl alcohol, from which it separated in rosette-like clusters of fine needles, melting sharply at 28°. On distillation the ester passed over at 245/15 mm. as a colourless oil, which solidified on cooling:

0·1390 gave 0·3236 CO_2 and 0·1187 H_2O. C = 63·5; H = 9·5.
0·1410 „ 0·3284 CO_2 „ 0·1208 H_2O. C = 63·5; H = 9·5.
$C_{19}H_{34}O_6$ requires C = 63·7; H = 9·5 per cent.

2·0986 required for hydrolysis 33·4 c.c. $N/2$ NaOH, the calculated amount for $C_{13}H_{25}(CO_2Me)_3$ being 35·1 c.c.

The hydrolysis of this ester yielded an acid which solidified in hard, warty masses, melting at 52—55°. The acid was subsequently dissolved in hot ethyl acetate, from which, on cooling, it separated in aggregates of fine needles, melting at 60°, and this melting point was not altered by further crystallisation. It is optically inactive:

0·1239 gave 0·2750 CO_2 and 0·0993 H_2O. C = 60·5; H = 8·9.
0·1106 „ 0·2458 CO_2 „ 0·0876 H_2O. C = 60·6; H = 8·8.
$C_{16}H_{28}O_6$ requires C = 60·8; H = 8·9 per cent.

This acid is a lower homologue of the tricarboxylic acid obtained by the oxidation of chaulmoogric acid, and, from considerations noted in the introductory portion of the paper, it is evidently n-*tridecane-aa′γ-tricarboxylic acid.*

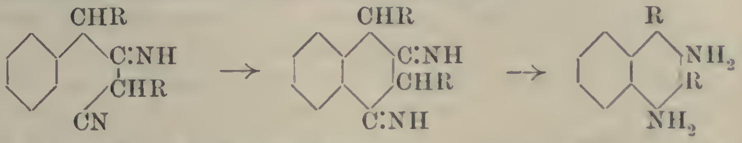
We desire to express our best thanks to Sir William H. Perkin, F.R.S., for having kindly determined for us the magnetic rotations recorded in this paper, and also to Professor A. Crum Brown, F.R.S., for having favoured us with a specimen of ethyl *n*-dodecanedicarboxylate.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

LVIII.—*The Formation and Reactions of Imino-compounds. Part III. The Formation of* 1:3-*Naphthylenediamine and its Derivatives from* o-*Toluonitrile.*

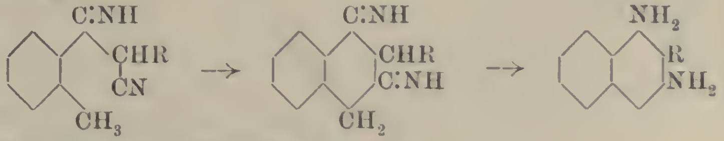
By ERNEST FRANCIS JOSEPH ATKINSON, HARRY INGHAM, and JOCELYN FIELD THORPE.

IN the preceding part of this series (Trans., 1906, **89**, 1906) it was demonstrated that derivatives of benzene containing a saturated side-chain of three carbon atoms substituted in the α-position by a nitrile group and in the β-position by an imino-group passed, on treatment with cold concentrated sulphuric acid, into derivatives of 1:3-naphthylenediamine, ring formation taking place between the carbon atom of the benzene ring in the *o*-position to the side-chain and the carbon atom of the nitrile group. It was further shown that this property was exhibited by other substituted compounds of this class, provided that a hydrogen atom remained attached to the α- and γ-carbon atoms respectively. The general formula representing this reaction can therefore be represented as follows:



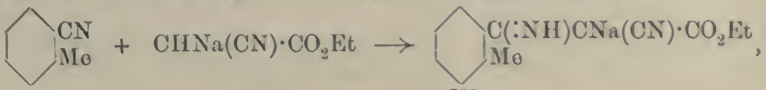
(R = hydrogen or substituting group).

In the present paper it is shown that derivatives of benzene containing a saturated side-chain of two carbon atoms substituted at the α-carbon atom by a nitrile group and at the β-carbon atom by an imino-group also pass under similar treatment into derivatives of 1:3-naphthylenediamine provided that the ortho-position in the benzene ring in respect to the side-chain is occupied by a methyl group. In this case, therefore, ring formation takes place between the carbon atom of the methyl group and the carbon atom of the nitrile group, and can be represented by the following general formula:



(R = hydrogen or substituting group).

Following along the lines adopted in the previous research in which the truth of the first generalisation mentioned above was established, it is apparent that one of the best compounds to test the truth of the second would be ethyl β-imino-α-cyano-β-o-tolylpropionate.



(I.) (II.) (III.)

the sodium derivatives of which (III) should be readily prepared by the condensation of o-toluonitrile (I) and the sodium compound of ethyl cyanoacetate (II).

There seems to be, however, very little tendency for an ortho-substituted nitrile such as o-toluonitrile to enter into condensation with ethyl sodiocyanoacetate to form an imino-compound. That this is due to the presence of the methyl group is shown by the fact that benzonitrile readily reacts with ethyl sodiocyanoacetate under the same conditions, forming the sodium derivatives of ethyl β-imino-α-cyano-β-phenylpropionate (IV),

$$C_6H_5\cdot CN + CHNa(CN)\cdot CO_2Et \longrightarrow \underset{\text{(IV.)}}{C_6H_5\cdot C(:NH)\cdot CNa(CN)\cdot CO_2Et},$$

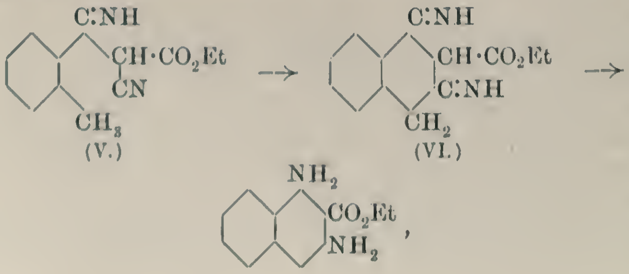
and that it is the ortho-position of the methyl group which is the inhibiting factor is indicated by the fact that E. v. Meyer (*J. pr. Chem.*, 1895, [ii], **52**, 113) prepared γ-imino-β-cyano-γ-*p*-tolylpropane, $C_6H_4Me\cdot C(:NH)\cdot CHMe(CN)$, by the action of sodium on a mixture of *p*-toluonitrile and propionitrile in dry ethereal solution.

It is possible by working under the conditions described in the experimental portion to obtain a small quantity of ethyl β-imino-α-cyano-β-*o*-tolylpropionate (I) by the interaction of *o*-toluonitrile and the sodium compound of ethyl cyanoacetate in alcoholic solution, but the yield under the most favourable conditions is scarcely 5 per cent. of the theoretical amount, and it is frequently less than this. A means was therefore sought by which this imino-compound could be prepared in larger quantities, and ultimately the following method was found to give slightly better results.

Many years ago v. Baeyer (*Ber.*, 1886, **19**, 428) succeeded in transforming ethyl succinylsuccinate into its di-imino-derivative by fusing this ethyl salt with dry ammonium acetate, a method which had been introduced shortly before by Knorr (*Ber.*, 1886, **19**, 46). On applying this reaction to ethyl cyano-*o*-toluoylacetate,

$$C_6H_4Me\cdot CO\cdot CH(CN)\cdot CO_2Et,$$

a compound which has been prepared by Haller (*Ber.*, 1888, **21**, 644) by the action of *o*-toluoyl chloride on the sodium derivative of ethyl cyanoacetate, it was found that its transformation into the imino-derivative could be partially effected by heating it in a sealed tube with dry ammonium acetate for several hours. The transformation is, however, only partial, and the conditions are difficult to regulate, since a slight variation in the temperature of the reaction brings about either a complete decomposition of both the keto- and the imino-ethyl salts or leaves the former entirely unacted on. Those conditions which are described in the experimental portion were found to give the best results; the yield, however, rarely exceeded 15 per cent. of the theoretical amount. Ethyl β-imino-α-cyano-β-*o*-tolylpropionate (V) is quantitatively converted into ethyl 1 : 3-naphthylenediamine-2-carboxylate (VI) on treatment with cold concentrated sulphuric acid :

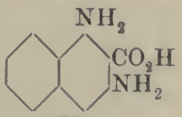


(V.)

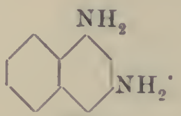
(VI.)

but the change does not take place quite so readily as in the case of ethyl β-imino-α-cyano-γ-phenylbutyrate dealt with in the previous paper. Thus it is necessary to leave the ethyl salt in contact with the strong acid for a slightly longer time before its transformation in the derivative of naphthalene is completely effected.

The identity of the product with ethyl 1 : 3-naphthylenediamine-2-carboxylate prepared by the action of concentrated sulphuric acid on ethyl β-imino-α-cyano-γ-phenylbutyrate (Trans., 1906, **89**, 1920) is shown not only by the fact that the two compounds possess the same melting point, but also by the fact that on hydrolysis they are both converted in the same 1 : 3-naphthylenediamine-2-carboxylic acid (VII), which on heating above its melting point is transformed into 1 : 3-naphthylenediamine (VIII) :

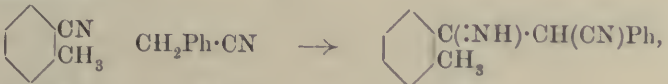


(VII.)



(VIII.)

The second compound chosen to illustrate the application of the second generalisation given on p. 579 was β-imino-α-cyano-α-phenyl-β-o-tolylethane (XI) :

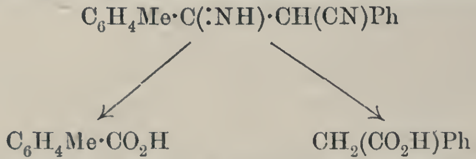


(IX.) (X.) (XI.)

which should be produced by the interaction of *o*-toluonitrile (IX) and benzyl cyanide (X) in the presence of sodium ethoxide.

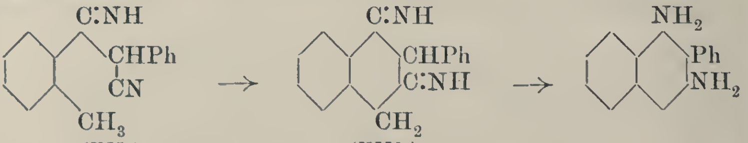
It is remarkable that this condensation should proceed with much greater readiness than the corresponding condensation of *o*-toluonitrile with ethyl cyanoacetate, and not only is this the case, but the by-products corresponding with those formed in the condensation of benzyl cyanide with its sodium derivative (compare Trans., 1906, **89**, 1930) are entirely absent when the condensation is carried out under the experimental conditions given on p. 588, and are apparently not formed even when the time of heating is increased beyond these limits. Since β-imino-α-cyano-α-phenyl-β-*o*-tolylethane prepared by this means could not be obtained in a solid condition even after being purified by fractional distillation, it was thought that it might be β-imino-α-cyano-αγ-diphenylpropane, $CH_2Ph\cdot C(:NH)\cdot CH(CN)Ph$, which had been formed by the condensation of benzyl cyanide with its sodium derivative and which it closely resembled both in appearance and properties, and that *o*-toluonitrile had not entered at all into the reaction.

This question was, however, answered by hydrolysing the imino-compound by means of alcoholic potash, when the formation of a mixture of *o*-toluic and phenylacetic acids, a method for the separation of which is given on p. 589, clearly showed that the condensation product was β-imino-α-cyano-α-phenyl-β-*o*-tolylethane, since the hydrolysis had evidently taken place in accordance with the scheme:



$$C_6H_4Me{\cdot}C(:NH){\cdot}CH(CN)Ph \rightarrow C_6H_4Me{\cdot}CO_2H \quad + \quad CH_2(CO_2H)Ph$$

Cold concentrated sulphuric acid instantly transforms β-imino-α-cyano-α-phenyl-β-*o*-tolylethane (XII) into 1 : 3-diamino-2-phenylnaphthalene (XIII):



(XII.) (XIII.)

The compound formed being identical with 1 : 3-diamino-2-phenylnaphthalene derived by the action of concentrated sulphuric acid on β-imino-α-cyano-αγ-diphenylpropane (compare Trans., 1906, 89, 1934).

During the course of these investigations two other condensations were studied, partly because the conditions of the formation of the condensation products were of importance in connexion with the condensations dealt with in this paper and partly because we wished to ascertain the action of concentrated sulphuric acid on imino-cyano-compounds containing a benzene ring to which a side-chain of less than three carbon atoms was attached and which had no substituting methyl group in the ortho-position in the benzene nucleus.

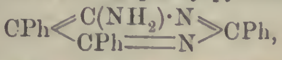
The first condensation investigated was that of benzonitrile with the sodium compound of ethyl cyanoacetate, which was studied in order to ascertain whether the failure of *o*-toluonitrile to enter into condensation with this ethyl salt was shared by other nitriles containing the nitrile group directly attached to the benzene ring. It was found, however, that a good yield of ethyl β-imino-α-cyano-β-phenylpropionate (IV) was obtained by this means, the reaction proceeding in accordance with the equation given on p. 579.

The other condensation was that of benzonitrile with the sodium derivative of benzyl cyanide, which was found to proceed in much the same way as the corresponding condensation of benzyl cyanide with its sodium derivative. In the condensation of benzyl cyanide with its sodium derivative it was shown that the product, after heating the condensing constituents on the water-bath for two hours, consisted of a mixture of about equal proportions of β-imino-α-cyano-αγ-diphenylpropane, α-cyano-αγ-dibenzylketone, and cyanbenzyline (compare Trans., 1906, **89**, 1931), ethylamine being at the same time eliminated.

The condensation of benzonitrile with the sodium compound of benzyl cyanide proceeds in precisely the same way, and after heating the constituents on the water-bath for two hours the product, which had a strong odour of ethylamine, was found to consist of about equal quantities of β-imino-α-cyano-αβ-diphenylethane,

$$CPh(\colon NH)\cdot CHPh\cdot CN,$$

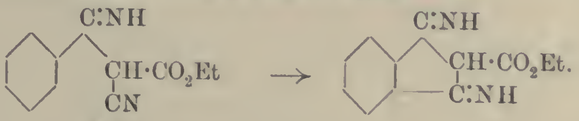
formed by the direct condensation of the two nitriles, cyanodeoxybenzoin, $COPh\cdot CHPh\cdot CN$, formed by the "alcoholysis" of the imino-compound, and 6-amino-2 : 4 : 5-triphenylpyrimidine,



$$CPh{<}\begin{matrix}C(NH_2)\cdot N\\ CPh{=\!=}N\end{matrix}{>}CPh,$$

formed by the condensation of two molecular proportions of benzonitrile with one of benzyl cyanide. It is remarkable that the corresponding condensation of *o*-toluonitrile with the sodium compound of benzyl cyanide already referred to on p. 581 should yield none of these secondary products, but should proceed directly with the formation of the true condensation product.

When ethyl β-imino-α-cyano-β-phenylpropionate (XIV) is treated with cold concentrated sulphuric acid no immediate reaction takes place although the solution becomes deep red. There is therefore no apparent tendency for this compound to be converted into the di-iminohydrindene derivative in accordance with the equation :



(XIV.)

When left in contact with the strong acid for some days the ethyl salt is completely converted into benzoylacetamide (XV), which can be obtained by pouring the strong acid solution into water :

$$CPh(\colon NH)\cdot CH(CN)\cdot CO_2Et. \longrightarrow COPh\cdot CH_2\cdot CO\cdot NH_2.$$

(XV.)

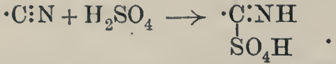
The same reaction is shown by β-imino-α-cyano-αβ-diphenylethane (XVI), which does not immediately react with concentrated sulphuric acid, but is completely converted after standing in the cold for three days into benzoylphenylacetamide (XVII). This product is also formed when the strong acid solution is poured into water.

$$CPh(\colon NH)\cdot CH(CN)Ph. \qquad COPh\cdot CHPh\cdot CO\cdot NH_2.$$

(XVI.) (XVII.)

There is, therefore, apparently no tendency for these compounds to be converted into derivatives of hydrindene although the formation in each of the above instances of a red condensation product, which was, however, too small for further investigation, seems to show that the reaction proceeds partly in that direction.

Experiments are, however, in progress which show that the action of concentrated sulphuric acid on nitriles gives rise to a definite addition product the formation of which may be probably represented by the general equation :

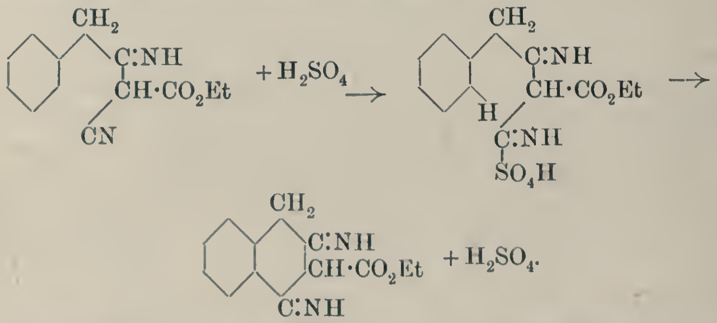


$$\cdot C\vdots N + H_2SO_4 \longrightarrow \cdot \underset{SO_4H}{\underset{|}{C}}\colon NH$$

In some cases, the details of which it is hoped will shortly be placed before the Society, these sulphuric acid addition products have been isolated as crystalline compounds which are found to be extremely reactive substances. The transformation of nitriles into the amides of the corresponding acids which has been observed by many investigators is, we find, caused by the action of water on the sulphuric acid addition product thus :

$$\cdot C(SO_4H)\colon NH + H_2O \longrightarrow \cdot CO\cdot NH_2 + H_2SO_4.$$

If, however, there is a tendency for the compound to enter into ring formation then sulphuric acid is eliminated thus :



In the two compounds ethyl *β*-imino-*α*-cyano-*β*-phenylpropionate (XIV) and *β*-imino-*α*-cyano-*αβ*-diphenylethane (XVI) it is this addition product with sulphuric acid which on treatment with water yields the amide, and it is therefore probable that on further investigation the conditions under which sulphuric acid is eliminated and the ring formed will be discovered. A complete study of the action of concentrated sulphuric acid on the nitriles and the conditions under which sulphuric acid is eliminated from them with the formation of carbon rings is in progress.

Ethyl-β-imino α-cyano-β-o-tolylpropionate,
$C_6H_4Me\cdot C(:NH)\cdot CH(CN)\cdot CO_2Et$.

(1) *Condensation of o-Toluonitrile with the Sodium Derivative of Ethyl Cyanoacetate.*—This condensation was effected in the following manner. 11·5 Grams of sodium were dissolved in 140 grams of absolute alcohol and the solution mixed with 57 grams of ethyl cyanoacetate, and subsequently with 59 grams of *o*-toluonitrile. The mixture was then heated on the water-bath until the white sodium derivative had completely dissolved, when it was transferred to a convenient number of thick-walled glass flasks which had been blown from ordinary Carius tubing. When these flasks had been three-parts filled with the liquid they were sealed in the ordinary way and heated in a paraffin bath at 120° for twenty-four hours. After cooling, the flasks were opened and the viscid gelatinous contents dissolved in dilute hydrochloric acid, the oil which then separated being extracted by means of ether. The ethereal solution was washed thoroughly with water and then with dilute aqueous sodium carbonate, being finally evaporated free from ether and the residue distilled with steam. By this means the whole of the unchanged *o*-toluonitrile was removed from the product, the residue, which solidified on cooling, being then separated by filtration. The ethyl salt was crystallised from absolute alcohol, being obtained in this way in white, glistening prisms melting at 135°:

0·1881 gave 0·4667 CO_2 and 0·1055 H_2O. $C=67·67$; $H=6·23$.

$C_{13}H_{14}O_2N_2$ requires $C=67·8$; $H=6·1$ per cent.

The yield of β-imino-α-cyano-β-*o*-tolylpropionate obtained by this process is exceedingly small, being scarcely 5 per cent. of the theoretical amount. Since no better yield was obtained by varying the conditions of the experiment, the following process was tried with slightly better success.

(2) *Action of Ammonium Acetate on Ethyl Cyano-o-toluoylacetate.*—Ethyl cyano-*o*-toluoylacetate has been prepared by Haller (*Ber.*, 1888, 21, 664) by the action of *o*-toluoyl chloride on the sodium compound of ethyl cyanoacetate. The details of the preparation of this substance which we found most convenient were as follows. Sixty grams of ethyl cyanoacetate were added to a solution of 11·5 grams of sodium dissolved in 140 grams of absolute alcohol and the white sodium derivative which separated on cooling filtered by the aid of the pump. After being washed with dry ether, the sodium compound was transferred to a large flask, ether added, and then, gradually, 77 grams of *o*-toluoyl chloride. A vigorous reaction started as soon as the acid chloride was added, and several times during the process of the addition

the contents of the flask had to be cooled under running water. When all the chloride had been added the ethereal solution was mixed with water, separated in the funnel, and after being thoroughly washed with water and dilute aqueous sodium carbonate, dried and evaporated free from ether. The oily residue, on being distilled under diminished pressure, passed over almost constantly at 180—181° (20 mm.) as a viscous, colourless oil which slowly solidified on standing. The solid was spread on a porous plate and crystallised from dilute alcohol, being obtained in colourless, glistening plates melting at 37°:

0·1789 gave 0·4420 CO_2 and 0·0931 H_2O. C = 67·38; H = 5·78.
$C_{13}H_{13}O_3N$ requires C = 67·5; H = 5·6 per cent.

The conversion of ethyl cyano-*o*-toluoylacetate into the corresponding imino-compound was effected by the action of ammonium acetate, the process being much the same as that employed by v. Baeyer (*Ber.*, 1886, **19**, 428) for the preparation of the di-imide of ethyl succinylsuccinate from ethyl succinylsuccinate, although in the present instance the change takes place with much greater difficulty, and the yield of the imino-compound is not nearly so satisfactory.

Twenty grams of ethyl salt were dissolved in 200 grams of dry melted ammonium acetate and the mixture heated in a sealed Carius tube at 120° for six hours. After this time the tube was opened and the liquid contents poured into cold water, when, on standing, a solid crystalline substance separated. This was collected, dried, and recrystallised twice from absolute alcohol, being thus obtained in white, glistening prisms melting at 135°:

0·1890 gave 0·4672 CO_2 and 0·1061 H_2O. C = 67·41; H = 6·23.
$C_{13}H_{14}O_2N_2$ requires C = 67·8; H = 6·1 per cent.

The compound was identical with ethyl β-imino-α-cyano-β-*o*-tolylpropionate prepared from *o*-toluonitrile and ethyl sodiocyanoacetate in the manner already described, and, although the yield of the ethyl salt is greater when working through the toluoylacetate than by direct condensation, yet in the former case it is far from satisfactory, being only 15 per cent. of the theoretical quantity from the amount of ethyl cyano-*o*-toluoylacetate used. In fact, the ethyl imino-salt appears to be an exceedingly difficult compound to prepare in any quantity.

Ethyl β-imino-α-cyano-β-*o*-tolylpropionate is readily soluble in hot alcohol and benzene, but sparingly so in these solvents in the cold; it is practically insoluble in light petroleum. The ethyl salt is not acted on by cold dilute aqueous alkalis, a fact which serves to distinguish it from the corresponding toluoyl derivative which is readily dissolved by these reagents.

*Hydrolysis of Ethyl β-Imino-α-cyano-β-*o*-tolylpropionate.*—As in the cases of similar ethyl imino-salts already dealt with, the constitution of the above substance was determined by means of alkaline hydrolysis previous to its transformation into the naphthalene ring in order that its formula might be established beyond question. The hydrolysis, which, as was to be expected, yielded a mixture of *o*-toluic and malonic acids, was carried out as follows. Seven grams of the ethyl salt were dissolved in a solution of 8 grams of potash dissolved in absolute methyl alcohol, and the solution heated on the water-bath until the odour of ammonia ceased to be apparent, and until a test portion on dilution with water remained clear, when it was poured into an evaporating basin and freed from methyl alcohol by evaporation on the water-bath. The solid residue was then dissolved in water and the solution acidified with hydrochloric acid, the oil which then separated and which rapidly solidified being separated by filtration. It crystallised from water in long, colourless needles melting at 102°, and was proved by the following analysis to be *o*-toluic acid :

0·2103 gave 0·5455 CO_2 and 0·1097 H_2O. C = 70·74 ; H = 5·79.
$C_8H_8O_2$ requires C = 70·6 ; H = 5·9 per cent.

The aqueous solution, after being filtered from the above acid, was extracted with ether in order to remove the last traces of *o*-toluic acid and was then evaporated to dryness on the water-bath, the solid residue being subsequently extracted in a Soxhlet apparatus with ether. The ethereal solution, after being dried, was evaporated free from ether, leaving a solid residue which, since it melted at 132° with decomposition and gave acetic acid on distillation, evidently consisted of malonic acid.

Formation of Ethyl 1 : 3-*Naphthylenediamine*-2-*carboxylate from Ethyl β-Imino-α-cyano-β-o-tolylpropionate.*—In order to effect this transformation 10 grams of the ethyl salt were added gradually to 30 grams of concentrated sulphuric acid cooled in ice. The solid rapidly dissolved and the solution became greenish-yellow in colour. It was allowed to stand for ten minutes after the last portion of the ethyl salt had been added, and was then poured on ice, when a clear yellow solution was obtained from which a yellow, crystalline precipitate separated on standing. This was collected by filtration, dissolved in a little cold water, the solution rendered alkaline with ammonia, and the resulting yellow precipitate collected by filtration. It crystallised from ether in golden-yellow plates melting at 108° :

0·2232 gave 0·5547 CO_2 and 0·1251 H_2O. C = 67·77 ; H = 6·22.
$C_{13}H_{14}O_2N_2$ requires C = 67·8 ; H = 6·1 per cent.

This substance was proved to be identical with ethyl 1 : 3-naphthylenediamine-2-carboxylate prepared by the action of concentrated sulphuric acid on ethyl β-imino-α-cyano-γ-phenylbutyrate, not only by direct comparison with this substance, but also by the fact that on hydrolysis with methyl-alcoholic potash it was converted into 1 : 3-naphthylenediamine-2-carboxylic acid melting at 85° with decomposition, which in its turn was transformed into 1 : 3-naphthylenediamine melting at 96°, on heating at 100° (compare Trans., 1906, **89**, 1920 *et. seq.*).

*β-Imino-α-cyano-α-phenyl-β-*o*-tolylethane.*—The condensation between benzyl cyanide and *o*-toluonitrile was effected in the following way. 11·5 Grams of sodium were dissolved in 140 grams of alcohol, the solution mixed with 59 grams of benzyl cyanide and then with 60 grams of *o*-toluonitrile. After the mixture had been heated on the water-bath for two and a half hours, water was added, and the oil which then separated extracted with ether. The ethereal solution after being washed with water was thoroughly shaken with hydrochloric acid (3 : 1)*, and finally with dilute aqueous sodium carbonate solution. It was then, without drying, freed from ether by evaporation, and the residue distilled in a current of steam.

When the product had been freed from unchanged benzyl cyanide and *o*-toluonitrile by this means, the residual oil was again extracted with ether, the ethereal solution dried and evaporated free from ether, the brown oil which remained being distilled under diminished pressure. Practically the whole of the product distilled constantly at 275° (20 mm.) as a viscous oil which did not show any tendency to crystallise:

0·1992 gave 0·6008 CO_2 and 0·1071 H_2O. $C = 82·25$; $H = 5·97$.

$C_{16}H_{14}N_2$ requires $C = 82·0$; $H = 6·0$ per cent.

It is possible that traces of β-imino-α-cyano-αγ-diphenylpropane, formed by the condensation of benzyl cyanide with its sodium derivative (compare Trans., 1906, **89**, 1930), may be mixed with this product and hence prevent it from crystallising. The compound seemed to be, however, a perfectly homogeneous substance distilling without any tendency to decompose under a pressure of 20 mm., whereas β-imino-α-cyano-αγ-diphenylpropane as already mentioned (*loc. cit.*) has to be rapidly distilled in small quantities under this pressure, otherwise decomposition sets in. β-Imino-α-cyano-α-phenyl-β-*o*-tolylethane, therefore, like its isomeride, appears to be a liquid under ordinary conditions.

*Hydrolysis of β-Imino-α-cyano-α-phenyl-β-*o*-tolylethane.*—The constitution of this substance was determined in the usual way by alkaline hydrolysis. Ten grams of the imino-compound were mixed with an alcoholic solution of 10 grams of potash and the mixture heated on the water-bath until a test portion on diluting with water remained clear. The alcohol was then completely eliminated by evaporation on the water-bath and the product, after being diluted with water, acidified with hydrochloric acid. The solid acids which were precipitated by this means were collected by filtration. They were separated by taking advantage of the fact that the calcium salt of *o*-toluic acid is less soluble in alcohol than the calcium salt of phenylacetic acid. The separation was effected as follows. The mixed acids were dissolved in water, and the solution mixed with excess of pure calcium carbonate. As soon as all effervescence had ceased the aqueous solution was separated from the unchanged carbonate by filtration and evaporated to a small bulk on the water-bath. When crystallisation commenced the solution was allowed to cool, and the mixed calcium salts which then crystallised out were separated by filtration and dried on a porous plate. For the purpose of separation the salts were dissolved in hot 90 per cent. alcohol (sp. gr. 0·81) and the solution allowed to cool. The calcium salt which then separated was collected and again recrystallised from alcohol, the process being repeated a third time, when a product was obtained which on reconversion into the acid gave a solid which melted at 100—102°. It was finally purified by recrystallisation from water and obtained in long needles melting at 104°, which from the following analysis evidently consisted of *o*-toluic acid:

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* To remove any pyrimidine derivative which may have been produced (compare Trans., 1906, **89**, 1931). In this case, however, no third layer was formed, indicating that no derivative of pyrimidine was present.

0·2106 gave 0·5218 CO_2 and 0·1235 H_2O. $C = 67·51$; $H = 6·51$.
$C_7H_8O_2$ requires $C = 67·8$; $H = 6·4$ per cent.

The calcium salt obtained on evaporating the mother liquors from the above separation to dryness was again treated in the same way, yielding a further quantity of the calcium salt of *o*-toluic acid. The ultimate residues were then reconverted into the acid, yielding a product which melted at 76° and which possessed the characteristic appearance and odour of phenylacetic acid.

Formation of 1:3-*Diamino-2-phenylnaphthalene from β-Imino-α-cyano-α-phenyl-β-o-tolylethane.*

In order to effect this transformation 20 grams of the imino-compound were added gradually to three times its weight of well-cooled, concentrated sulphuric acid.

The solution, which became greenish-yellow in colour, was allowed to stand for two minutes after the last quantity of the imino-compound had been added, and was then poured into a large volume of water. The solution thus obtained, after being filtered to remove a small quantity of insoluble matter, was rendered alkaline with ammonia, and the resulting copious precipitate isolated by filtration. By crystallisation from methyl alcohol the base was obtained in glistening plates melting at 116°:

0·2085 gave 0·6265 CO_2 and 0·1137 H_2O. C = 81·95; H = 6·05.

$C_{16}H_{14}N_2$ requires C = 82·0; H = 6·0 per cent.

This base was proved to be identical with that derived from β-imino-α-cyano-αγ-diphenylpropane (Trans., 1906, 89, 1934), not only by direct comparison with the substance, but also by the fact that on treatment with acetyl chloride it was converted into the same diacetyl derivative melting at 267°.

Ethyl β-Imino-α-cyano-β-phenylpropionate.

The condensation between benzonitrile and the sodium compound of ethyl cyanoacetate was effected in the following way. 11·5 Grams of sodium were dissolved in 140 grams of alcohol and the solution mixed with 57 grams of ethyl cyanoacetate, and then with 52 grams of benzonitrile, the whole being heated on the water-bath for ten hours. At the end of this time the contents of the flask had become almost solid, owing to the formation of a brown, gelatinous solid. Water was added, and the solution after being strongly acidified with hydrochloric acid was extracted thoroughly with ether.

The ethereal extract was washed with water and then with dilute sodium carbonate solution, being finally evaporated free from ether and distilled in a current of steam until all unchanged benzonitrile had passed over. The residue, which consisted of a dark brown, heavy oil, solidified on cooling. It was collected by filtration and crystallised from alcohol, being obtained in lustrous plates melting at 125°:

0·1945 gave 0·4744 CO_2 and 0·1007 H_2O. C = 66·52; H = 5·71.

$C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6 per cent.

The compound closely resembles both in appearance and properties its next higher homologue, ethyl β-imino-α-cyano-γ-phenylbutyrate, and also melts at the same temperature as this substance. Its constitution was determined by hydrolysing it with an alcoholic solution of potash, the hydrolysis being effected by boiling the ethyl salt with a methyl-alcoholic solution of 1½ times the calculated quantity of potash until a test portion was completely soluble in water; the alcohol was then evaporated and the residue, after being diluted with water, acidified by means of hydrochloric acid. The white, crystalline precipitate which then separated was collected by the aid of the pump and recrystallised from hot water. It melted at 121° and gave all the reactions of benzoic acid. The aqueous solution was evaporated to dryness and the residue extracted in a Soxhlet apparatus with ether. The dried ethereal solution on evaporation yielded malonic acid melting at 132°.

Action of Concentrated Sulphuric Acid on Ethyl β-Imino-α-cyano-β-phenylpropionate.

Concentrated sulphuric acid has no immediate action on ethyl β-imino-α-cyano-β-phenylpropionate, and the ethyl salt can be dissolved in the strong acid without apparent change, since it can be recovered on pouring the solution into water. If, however, the solution is left to stand for some days, the ethyl salt is converted into benzoylacetamide. Ten grams of the imino-compound were added gradually to three times its weight of concentrated sulphuric acid, and the solution, after standing for three days, poured into a large volume of water. The solution became deep red, and a red, flocculent precipitate separated on standing. This was collected by filtration, but the quantity proved too small for further investigation. The filtrate was rendered alkaline with ammonia and extracted with ether, the ethereal solution being dried and evaporated free from ether. The residual solid was crystallised from a little water and obtained in lustrous plates melting at 114—115° with evolution of gas at 160°:

0·1661 gave 0·4037 CO_2 and 0·0831 H_2O. C = 66·28 ; H = 5·56.

$C_9H_9O_2N$ requires C = 66·3 ; H = 5·5 per cent.

The compound is evidently identical with benzoylacetamide,

$$COPh{\cdot}CH_2{\cdot}CO{\cdot}NH_2,$$

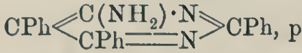
which Obrégia (*Annalen*, 1891, 266, 332) prepared by the action of concentrated sulphuric acid on ω-cyanoacetophenone and described as melting at 111—113°.

Condensation of the Sodium Compound of Benzyl Cyanide with Benzonitrile.

The interaction of benzyl cyanide and benzonitrile in the presence of metallic sodium has already been studied by a number of investigators. The object of the present experiments was to determine whether the condensation between these two nitriles in the presence of sodium ethoxide would proceed in the same way as the corresponding condensation of benzyl cyanide with its sodium derivative (compare Trans., 1906, 89, 1930).

11·5 Grams of sodium were dissolved in 140 grams of alcohol and a mixture of 58 grams of benzyl cyanide and 52 grams of benzonitrile added, the whole being heated on the water-bath for three hours. During the time of heating the odour of ethylamine was very strong, showing that the imino-group was being "hydrolysed" in the same manner as in the corresponding experiment with benzyl cyanide. After being heated for the time stated, the contents of the flask, which were quite solid, were treated with water and extracted with ether, the ethereal solution after being washed with water and dilute sodium carbonate solution evaporated free from ether, and the residue distilled in a current of steam. When all the unchanged benzyl cyanide and benzonitrile had passed over, the viscid, oily residue was extracted by means of ether, and the ethereal solution thoroughly shaken with a mixture of three parts of concentrated hydrochloric acid to one of water. By this means a large quantity of a semi-solid hydrochloride which was extracted from the ethereal solution was separated in the funnel and converted into the free base by treatment with sodium carbonate solution. The white product thus obtained gave, on crystallisation from alcohol, fine, white needles melting at 177°:

$0{\cdot}1563$ gave $0{\cdot}4698$ CO_2 and $0{\cdot}0782$ H_2O. $C = 81{\cdot}98$; $H = 5{\cdot}55$.
$C_{22}H_{17}N_3$ requires $C = 81{\cdot}7$; $H = 5{\cdot}3$ per cent.

This substance is evidently identical with 6-amino-2 : 4 : 5-triphenyl pyrimidine,  $CPh<\begin{matrix}C(NH_2)\cdot N\\ CPh{=}{=}{=}N\end{matrix}>CPh$, prepared by Wache (*J. pr. Chem.*, 1889, [ii], 39, 253) by the action of benzonitrile on the sodium compound of dibenzyl cyanide.

The ethereal solution, after the separation of the hydrochloride of the above base, was dried and the ether evaporated. The solid residue after crystallisation twice from alcohol was obtained in colourless plates melting at 146°:

$0{\cdot}1719$ gave $0{\cdot}5167$ CO_2 and $0{\cdot}850$ H_2O. $C = 81{\cdot}96$; $H = 5{\cdot}52$.
$C_{15}H_{12}N_2$ requires $C = 81{\cdot}8$; $H = 5{\cdot}4$ per cent.

This compound is evidently β-imino-α-cyano-$\alpha\beta$-diphenylethane, identical with the compound prepared by E. v. Meyer (*J. pr. Chem.*, 1895, [ii], 52, 116) by the action of ammonia on cyanodeoxybenzoin and by Walther and Schickler (*J. pr. Chem.*, 1897, [ii], 55, 320) by the action of sodium on a mixture of benzyl cyanide and benzonitrile in ethereal solution.

The alcoholic mother liquors from the recrystallisation of the above imino-compound were evaporated to a small bulk, when a further quantity of β-imino-α-cyano-$\alpha\beta$-diphenylethane was obtained. The ultimate filtrate was then evaporated to dryness and the solid residue crystallised from light petroleum (b. p. 60—70°), yielding white needles melting at 90°:

$0{\cdot}1812$ gave $0{\cdot}5408$ CO_2 and $0{\cdot}851$ H_2O. $C = 81{\cdot}38$; $H = 5{\cdot}21$.
$C_{15}H_{11}ON$ requires $C = 81{\cdot}4$; $H = 5{\cdot}0$ per cent.

This compound is evidently α-cyanodeoxybenzoin,

$COPh{\cdot}CH(CN)Ph$,

first prepared by E. v. Meyer (*loc. cit.*) by the interaction of ethyl benzoate and benzyl cyanide in the presence of sodium ethoxide.

Action of Concentrated Sulphuric Acid on β-Imino-α-cyano-αβ-diphenylethane.

The action of concentrated sulphuric acid on the imino-compound does not lead to the closing of the ring, but only transforms the nitrile into the amide of the corresponding ketone.

Five grams of the imino-compound were dissolved in three times its weight of concentrated sulphuric acid and the solution allowed to stand in the cold for forty-eight hours. On pouring the acid into water a clear solution was obtained, from which a crystalline precipitate separated on standing.

This was collected by filtration and recrystallised from alcohol, being obtained in small needles melting at 178°:

0·1626 gave 0·4484 CO_2 and 0·0866 H_2O. C = 75·21; H = 5·96.

$C_{15}H_{13}O_2N$ requires C = 75·3; H = 5·8 per cent.

This compound is evidently identical with benzoylphenylacetamide, $COPh\cdot CHPh\cdot CO\cdot NH_2$, which Walther and Schickler (*J. pr. Chem.*, 1897, [ii], **55**, 314) prepared by the action of concentrated sulphuric acid on α-cyanodeoxybenzoin and described as melting at 172—173°.

Much of the expense entailed by this research has been met by a grant from the Government Grant Committee of the Royal Society, for which we desire to express our indebtedness.

MANCHESTER UNIVERSITY.

LIX.—*The Velocity of Hydrolysis of Aliphatic Amides.*

By JAMES CODRINGTON CROCKER, M.A.

THIS work was undertaken in order to compare the reactivities of the homologous fatty amides, and to investigate the relation between reactivity and constitution in this case. The amides are interesting in view of their tautomeric behaviour. They may function either as "amido" compounds or as the corresponding hydroxyimino-derivatives. If they exist as the latter, they would be expected, from analogy with hydroxylic derivatives generally, to be associated in the liquid state, and, moreover, to be electrolytes in associated solvents.

The conductivities of the amides were examined by Hantzsch and

Büchner (*Ber.*, 1901, **34**, 3142), and these substances were found to be very feeble electrolytes and to be quite neutral in reaction. On the other hand, fused acetamide is an ionising medium, and produces dissociation of metallic salts (Walker and Johnson, Trans., 1905, **87**, 1597). The amides also show abnormal cryoscopic behaviour in naphthalene solution. These facts point to a tendency to molecular association, and hence suggest the presence of the hydroxyl group. The question was elucidated by the work of Hantzsch and Voegeler (*loc. cit.*) on glycolliminohydrin, the desmotrope of glycollamide. This substance was first isolated by Eschweiler (*Ber.*, 1897, **30**, 998) from the products of the action of water on glycollonitrile at 130°. It differs widely in its properties from glycollamide. It is a comparatively strong electrolyte, and ebullioscopic determinations in absolute alcohol showed that it possessed a doubled molecule. It is decomposed with difficulty by hydrochloric acid, and it forms a hydrochloride and a sodium salt. It is evidently the hydroxylimino-derivative, and the contrast between the properties of this substance and those of the ordinary amides renders the "amido" formula for the latter very probable.

In the determination of the reactivities of the amides, the reaction utilised was that of the hydrolysis of the amides by dilute hydrochloric acid. The case of acetamide was worked out by Ostwald (*J. pr. Chem.*, 1883, **27**, 1). He used this reaction in measurements of the relative strengths of acids. The change is represented by the equation

$$CH_3{\cdot}CO{\cdot}NH_2 + H_2O + HCl = CH_3{\cdot}CO_2H + NH_4Cl,$$

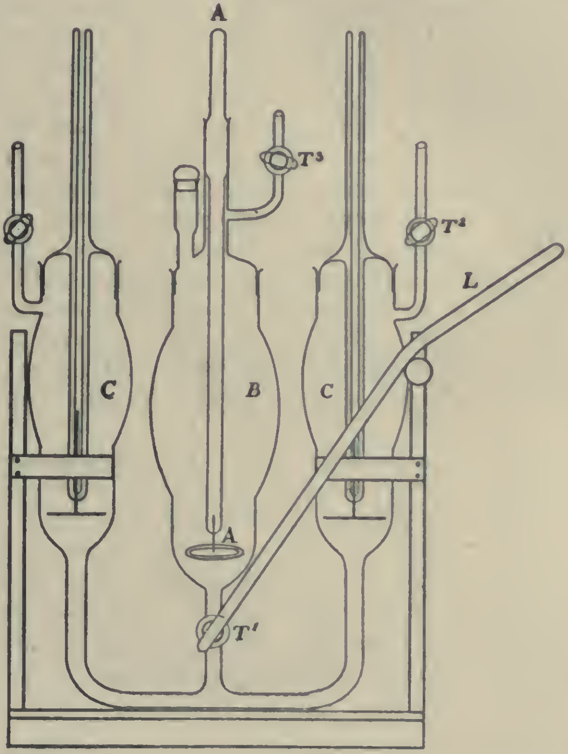
and the reaction should be of the second order.

The amide was heated with the equivalent quantity of acid in 2/3 *N*-solution to 65° or 100°, and the ammonium salt formed was estimated by decomposition with sodium hypobromite solution, corrections being applied for the solubility of nitrogen and the slight action of hypobromite on acetamide. The ratio of the reciprocals of the times for half completion of the reaction gave the relative strengths of the acids. In the present investigation, the method of electrical conductivity was used for the determination of the amount of chemical change. This is a convenient process, since the relatively large change of conductivity, due to the fall in concentration of the hydrogen ions, permits of accurate estimation of the composition of the solution.

The apparatus consisted of a post-office box fitted up as a Wheatstone bridge and used in conjunction with an induction coil and telephone receiver according to the Kohlrausch method. The contact-breaker of the coil was made especially light so as to give a high-frequency note in the telephone. The indications are sharpest when all four arms of the bridge are of the same resistance. With a reaction which takes an hour to half-completion, and with 500 ohms in each arm, the accuracy in the time-readings is about two to three seconds. This error is much less than that caused by the variation of 1/20° in the temperature.

The time to a given resistance is determined by observing the instant when the removal of the one-ohm plug produces no change in the intensity of the sound in the receiver. The resistance at this moment is then 0·5 ohm greater than when the plug is in the box.

FIG. 1.



The electrolytic cell is constructed so that mixing can be effected rapidly at the temperature of the thermostat.

The amide solution is placed in the central reservoir *B* and the hydrochloric acid in the cell *CC*. When the temperature is constant the taps T_2T_2 are opened. The lever *L* is pushed over until tap T_1 is opened and then suction is applied at tap T_3. The acid is thus drawn into the central vessel, and is mixed rapidly with the amide solution by using the stirrer *A*. Then the solution is rapidly passed to and from the cell *CC* for a minute or so, stirring at intervals. Finally, the mixture is driven over into CC and the resistance of the solution taken from time to time. This type of cell has been used also in determinations of the molecular conductivity of hydrochloric acid and of ammonium chloride at different dilutions with satisfactory results. It is convenient for dilution in hot solution where loss by evaporation is troublesome.

All the experiments in the first section of the paper were done at 63·2°. The thermostat was fitted with a long, narrow, cylindrical mercury thermo-regulator. A layer of paraffin was used in the bath to prevent the disturbing effects due to evaporation. The stirring gear was worked by a small electric motor. Without these arrangements accurate measurements are difficult, owing to the large influence of temperature on conductivity and velocity of reaction.

The general mode of procedure in the determination of a velocity-constant is as follows: the conductivity-time curves for a series of synthetical mixtures of amide, hydrochloric acid, ammonium chloride, and acetic acid were determined, and by extrapolation to $t=0$ the initial specific conductivity of each mixture was found. These values were plotted against the corresponding concentrations, and the resulting curve served to standardise the conductivity-time curve of the original mixture of acid and amide, and gave the concentration-time curve required. As the resistance-time curves were found to be nearly straight lines over moderate ranges, they were used for the extrapolations.

It was shown by experiment that in all cases the curves drawn between time and the reciprocal of concentration approximated very closely to straight lines up to about 40 per cent. of the reactions. Hence it follows that the reactions are all of the second order. The deviations from the linear relation outside the above range are due to the accumulation of ammonium chloride in the solutions and its effect in increasing the "strength" of the hydrochloric acid.

Let the equation of this curve in a given case be:

$$1/C = P + Qt + Rt^2 + \dots\dots\dots\dots\dots\dots$$

By differentiation:

$$-\frac{1}{C^2}\cdot\frac{dc}{dt} = Q + 2Rt + \dots\dots\dots\dots\dots\dots$$

so that $$-\frac{dc}{dt} = C^2(Q + 2Rt + \dots\dots\dots\dots) = KCC^1,$$

hence $$K = \frac{C}{C^1}(Q + 2Rt + \dots\dots\dots\dots),$$

where C is the concentration of the amide, C^1 that of the ionic hydrochloric acid, and K is the velocity-constant. Within the limits specified the curve is very approximately a linear function, and hence $R=0$ and

$K=\frac{C}{C^1}.Q$, where Q is the mean differential-coefficient of the curve within the range considered. The ionic concentration C^1 of the hydrochloric acid was calculated from the conditions of isohydry. As no simple accurate algebraic relation exists between dilution and dissociation in the case of strong electrolytes, the question was solved graphically.

Consider a cube of 1 c.c. volume divided into two parts by a movable semi-permeable partition. Let both compartments be filled first with hydrochloric acid and let the molecular concentration be C_0. Now let a fraction, β, of the acid be replaced by the equivalent amount of ammonium chloride in the solution—the partition dividing the two electrolytes. If v is the volume of the ammonium chloride solution and $1-v$ that of the acid, $x=\frac{\beta C_0}{v}$ and $x^1=\frac{(1-\beta)C_0}{1-v}$ are the molecular concentrations of the chloride and acid respectively. The corresponding ionic concentrations are read off from a curve between ionic concentrations and molecular concentrations, and the results are plotted against v for several positions of the partition on either side of the point at which the ionic concentrations of chloride and acid become identical. The intersections of the resulting lines give the isohydric conditions. These are the series of short intersecting lines in the diagrams. The ionic concentration of the acid in the solution as a whole, when the partition is removed and the solutions mixed, is given by $(1-v)C_i$, where C_i is the common ionic concentration in the isohydric solutions of chloride and acid respectively.

The lower oblique curves in the diagrams show the variation of the concentration of the acid ions with the proportion of chloride replacing the acid.

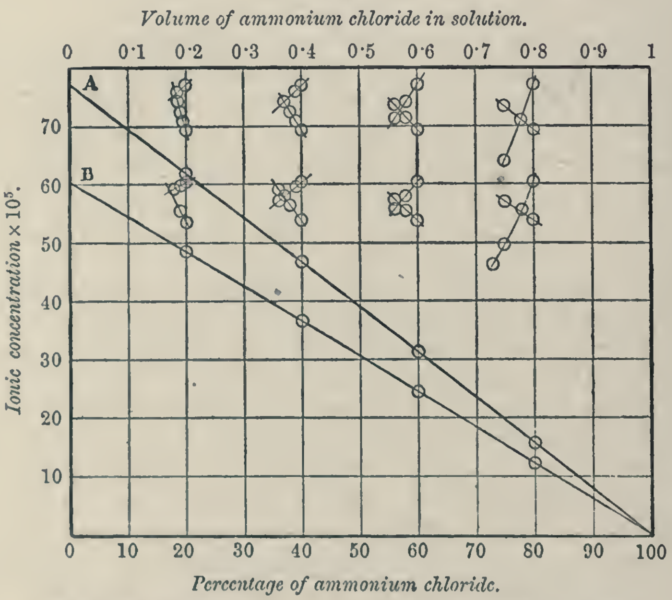
The graphs for N and $3/4N$ strengths at 63·2° are shown on p. 598; they are very nearly straight lines.

The water used in the work was prepared by redistilling ordinary distilled water from alkaline permanganate and passing the vapour through phosphoric acid. It was condensed in a tin condenser. One distillation under ordinary conditions gave water of specific conductivity $2{\cdot}7\times10^{-6}$ mhos per c.c., which is of the requisite degree of purity. The hydrochloric acid used was prepared by passing the gas obtained from ordinary "pure" hydrochloric acid and sulphuric acid into pure water. The ammonium chloride was twice recrystallised from distilled water.

(*a*) *The Reactivities of the Amides at Constant Temperature.*

Acetamide.—The substance was purified by rapidly crystallising thrice from acetone, in which it is very soluble. It was then odourless.

FIG. 2.



A. Normal solutions. *B.* 3/4-Normal solutions.

I.

20 c.c. 2*N*-amide. 20 c.c. 2*N*-acid.
$\theta = 63 \cdot 2°$. $Q = 16 \cdot 28$.

Initial concentration = *N*.

t.	σ.	$C \times 10^5$.	$C' \times 10^5$.	$K = c/c'Q$.
5·0	0·3945	92·50	71·40	21·09
7·50	0·3880	89·00	68·70	21·09
13·03	0·3743	82·00	63·30	21·09
18·83	0·3617	76·20	58·90	21·07
24·45	0·3499	70·80	54·90	21·00
30·88	0·3388	66·10	51·30	20·98
34·16	0·3335	63·80	49·60	20·94
37·62	0·3283	61·60	47·80	20·98
41·16	0·3234	59·60	46·30	20·95
44·78	0·3185	57·70	44·90	20·93
48·45	0·3139	55·55	43·30	20·91
		Mean *K*	=	21·00

$\sigma^{0} = 0 \cdot 4000$, $\sigma^{0 \cdot 08} = 0 \cdot 3935$,
$\sigma^{0 \cdot 16} = 0 \cdot 3784$, $\sigma^{0 \cdot 32} = 0 \cdot 3430$,
$\sigma^{0 \cdot 72} = 0 \cdot 2490$, $\sigma^{0 \cdot 64} = 0 \cdot 2870$.

II.

40 c.c. *N*/2-acid. 40 c.c. *N*/2-amide.
$\theta = 63 \cdot 2°$. $Q = 20 \cdot 15$.

Initial concentration = *N*/4.

t.	σ.	$C \times 10^5$.	$C' \times 10^5$.	$K = c/c'Q$.
12·42	0·1320	23·53	21·35	22·21
14·16	0·1314	23·31	21·15	22·21
22·33	0·1286	22·50	20·42	22·22
30·42	0·1258	21·64	19·65	22·19
39·39	0·1233	20·94	19·05	22·15
48·08	0·1207	20·16	18·35	22·14
57·16	0·1183	19·46	17·70	22·15
76·42	0·1138	18·06	16·40	22·20
96·92	0·1095	16·80	15·32	22·10
119·42	0·1056	15·62	14·25	22·09
142·42	0·1020	14·47	13·25	22·01
		Mean *K*	=	22·15

$\sigma^{0} = 0 \cdot 1366$, $\sigma^{0 \cdot 5} = 0 \cdot 0954$, $\sigma^{1} = 0 \cdot 0547$.

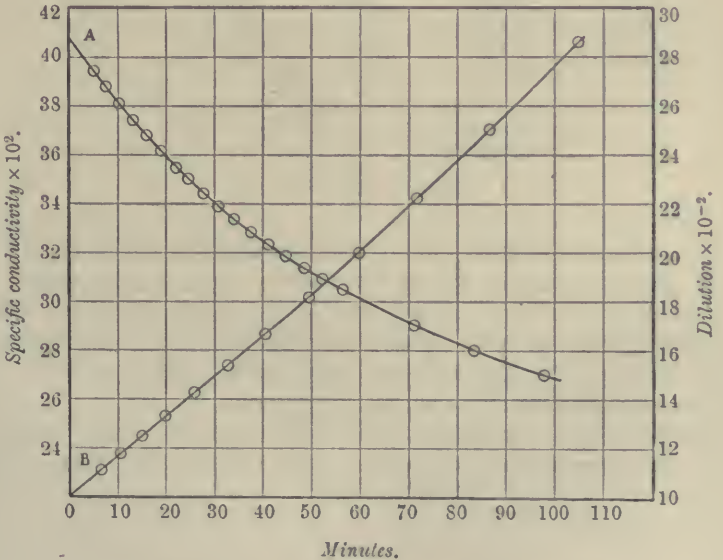
Range 0 to 40 per cent.

In the above and succeeding tables:

θ = temperature;
t = time in minutes;
C = concentration of amide in gram-equivalents per c.c.;
C^1 = ionic concentration of acid;
σ = specific conductivity of solution in mhos per c.c.;
K = velocity-constant;
Q = rate of change of dilution of amide in c.c. per minute;
β = fraction of amide decomposed;
σ^{β} = specific conductivity of solution when fraction β of amide is decomposed.

Thus in the table above, $\sigma^{0\cdot32} = 0\cdot3430$ indicates that when 32 per cent. of the reaction has taken place the specific conductivity of the solution is 0·3430. Each value for σ^{β} is determined by extrapolation of a different resistance-curve, and to economise space this abbreviated notation is used. The curves for N-acetamide solution and N-hydrochloric acid are shown below.

FIG. 3.



A. Conductivity : time. *B.* Dilution : time.

The curve A is the conductivity-time relation and B is the derived dilution-time curve. Up to 44 per cent. the latter curve is practically a straight line; but beyond that marked curvature sets in. This shows that the ordinary bimolecular relation is followed within these limits, but that beyond the range the rate of reaction is greater than that calculated on the assumption that the concentration of the hydrogen ions is a linear function of the "degree of reaction." In other words, the strength of the acid is increased by the presence of the neutral salt in solution. The degree of constancy in the value of K is shown by reference to the numerical results.

Propionamide.—The amide obtained from Kahlbaum was twice recrystallised from acetone. It was then free from acid.

20 c.c. $2N$-amide. 20 c.c. $2N$-hydrochloric acid.

$\theta = 63·2°$. $Q = 19·90$.

Initial concentration $= N$.

t.	σ.	$C \times 10^5$.	$C' \times 10^5$.	$K = c/c'Q$.
5·88	0·3791	90·25	69·60	25·80
10·47	0·3643	83·30	64·40	25·77
15·10	0·3513	77·40	59·90	25·72
19·88	0·3392	72·10	55·80	25·72
24·88	0·3279	67·20	52·10	25·68
27·50	0·3225	64·70	50·30	25·60
30·15	0·3173	62·60	48·60	25·64
32·87	0·3123	60·30	46·90	25·59
35·75	0·3075	58·40	45·40	25·60
38·87	0·3028	56·30	43·80	25·58
41·87	0·2982	54·40	42·40	25·53
			Mean K =	25·66

$\sigma^{0} = 0·3992$, $\sigma^{0·2} = 0·3742$, $\sigma^{0·24} = 0·3478$.
$\sigma^{0·36} = 0·3213$, $\sigma^{0·48} = 0·2929$, $\sigma^{0·64} = 0·2547$.
$\sigma^{0·8} = 0·2163$.

Range 0 to 46 per cent.

Here again the reaction follows the bimolecular relation closely, K being nearly constant within the limits. The slight tendency of the constant to diminish with increasing time in this and other experiments represents the margin of error introduced by taking the mean slope of the dilution-time curve to be equal to the true differential-coefficient of the curve at each point.

It will be noted that propionamide is more reactive than acetamide. With the exception of formamide, it is the most reactive of the series.

n-*Butyramide.*—Kahlbaum's preparation was used. Owing to the solubility, solutions of greater strength than $1\frac{1}{2}N$ could not be conveniently used. In experiment II, $N/4$ solutions were used and a larger cell employed.

I.

20 c.c. $1\frac{1}{2}N$-acid. 20 c.c. $1\frac{1}{2}N$-amide.

$\theta=63\cdot2°$. $Q=9\cdot56$.

Initial concentration $=\frac{3}{4}N$.

t.	σ.	$C\times10^5$.	$C'\times10^5$.	K.
3·53	0·3156	73·35	59·10	11·87
11·28	0·3065	69·50	56·00	11·86
19·36	0·2975	66·03	53·20	11·84
27·30	0·2892	62·90	50·08	12·01
31·37	0·2853	61·32	49·60	11·82
36·37	0 2814	59·56	48·25	11·81
40·50	0·2776	58·16	47·05	11·82
45·15	0·2740	72·46	46·00	11·79
49·82	0·2704	55·20	44·85	11·79
54·50	0·2670	54·05	43·90	11·76
59·32	0·2636	52·65	42·80	11·76

Mean K = 11·83

$\sigma^0=0\cdot3199$, $\sigma^{0\cdot3}=0\cdot2634$.
$\sigma^{0\cdot5}=0\cdot2255$, $\sigma^1=0\cdot1305$.

Range 0 to 30 per cent.

II.

35 c.c. $N/2$-acid. 35 c.c. $N/2$-amide.

$\theta=63\cdot2°$. $Q=10\cdot78$.

Initial concentration – $N/4$.

t.	σ.	$C\times10^5$.	$C'\times10^5$.	K.
9·08	0·1344	24·39	22·15	11·87
14·16	0·1332	24·08	21·87	11·87
19·66	0·1320	23·73	21·57	11·86
25·00	0·1309	23·42	21·30	11·85
35·08	0·1286	22·83	20·74	11·87
40·16	0·1275	22·55	20·50	11·85
45·24	0·1264	22·29	20·26	11·85
50·81	0·1253	21·99	20·00	11·85
59·66	0·1237	21·52	19·57	11·85
62·92	0·1233	21·37	19·40	11·87

Mean K = 11·86

$\sigma^0=0\cdot1374$, $\sigma^{0\cdot1}=0\cdot1273$.
$\sigma^{0\cdot5}=0\cdot0936$, $\sigma^1=0\cdot0540$.

Range 0 to 15 per cent.

There is a marked decrease in the reactivity in passing from propionamide to butyramide.

iso*Butyramide.*—Kahlbaum's preparation was used.

I.

20 c.c. $1\frac{1}{2}N$-amide. 20 c.c. $1\frac{1}{2}N$-acid.

$\theta=63\cdot2°$ $Q=12\cdot04$.

Initial concentration $=\frac{3}{4}N$.

t.	σ.	$C\times10^5$.	$C'\times10^5$.	K.
6·16	0·3222	71·18	57·25	14·97
7·97	0·3194	70·04	56·40	14·95
12·13	0·3136	67·70	54·60	14·93
15·92	0·3083	65·60	53·00	14·90
19·50	0·3033	62·80	51·60	14·88
23·55	0·2986	61·93	50·10	14·88
31·75	0·2893	58·32	47·20	14·87
37·97	0·2828	55·92	45·30	14·85
42·23	0·2785	54·32	44·00	14·86
46·83	0·2744	52·80	42·90	14·81
51·50	0·2705	51·20	41·60	14·82

Mean K = 14·89

$\sigma^0=0\cdot3317$, $\sigma^{0\cdot2}=0\cdot2937$, $\sigma^{0\cdot4}=0\cdot2533$,
$\sigma^{0\cdot5}=0\cdot2331$, $\sigma^1=0\cdot1319$.

Range 0 to 32 per cent.

II.

20 c.c. $1\frac{1}{2}N$-amide. 20 c.c. $1\frac{1}{2}N$-acid.

$\theta=63\cdot2°$. $Q=12\cdot04$.

Initial concentration $=\frac{3}{4}N$.

t.	σ.	$C\times10^5$.	$C'\times10^5$.	K.
5·62	0·3244	71·60	57·60	14·92
9·28	0·3189	69·40	55·85	14·91
12·88	0·3136	67·33	54·20	14·91
18·42	0·3058	64·54	52·00	14·90
22·42	0·3010	62·53	50·45	14·87
26·30	0·2962	60·85	49·10	14·87
30·47	0·2916	58·99	47·60	14·87
34·72	0·2870	57·23	46·25	14·85
39·12	0·2828	55·60	45·00	14·83
43·42	0·2785	54·05	43·85	14·79
52·28	0·2705	51·07	41·40	14·80

Mean K = 14·87

$\sigma^0=0\cdot3317$, $\sigma^{0\cdot2}=0\cdot2937$, $\sigma^{0\cdot4}=0\cdot2533$,
$\sigma^{0\cdot5}=0\cdot2331$, $\sigma^1=0\cdot1319$.

Range 0 to 32 per cent.

*iso*Butyramide, contrary to expectation, is more reactive than butyramide.

iso*Valeramide.*—Kahlbaum's preparation was used. Solutions stronger than $3/4N$ cannot conveniently be used.

20 c.c. $\frac{3}{4}N$-acid. 20 c.c. $\frac{3}{4}N$-amide.
$\theta = 63{\cdot}2°$. $Q = 2{\cdot}875$.
Initial concentration $= 3/8N$.

t.	σ.	$C \times 10^5$.	$C' \times 10^5$.	K.
6·0	0·1849	37·24	32·00	3·347
25·0	0·1822	36·50	31·40	3·343
43·0	0·1804	35·84	30·85	3·341
60·50	0·1787	35·21	30·30	3·342
94·0	0·1753	34·01	29·25	3·343
111·0	0·1737	33·50	28·80	3·345
127·0	0·1726	33·00	28·40	3·342
165·0	0·1690	31·85	27·45	3·336
174·0	0·1682	31·55	27·20	3·326
206·0	0·1660	30·68	26·40	3·342
225·0	0·1645	30·12	25·95	3·338
245·0	0·1631	29·63	25·50	3·342
			Mean K =	3·341

$\sigma^0 = 0{\cdot}1847$, $\sigma^{0{\cdot}25} = 0{\cdot}1586$, $\sigma^{0{\cdot}5} = 0{\cdot}1308$, $\sigma^1 = 0{\cdot}0741$.
Range 0 to 21 per cent.

Owing to the small solubility of valeramide and the low velocity-constant, some difficulty was experienced in determining the equilibrium points with the usual degree of accuracy.

The velocity-constant of valeramide is by far the smallest of the series and is remarkable in view of its constitution and relation to the members on either side of it in the series.

Capronamide.—The amide is not very soluble in cold water. Kahlbaum's preparation was used, and was made up so that it was exactly $N/2$ when at 66°, and the solutions were measured out while hot into the apparatus ready in the thermostat. It was noticed that after a few minutes the hot solution became slightly turbid, possibly owing to the separation of a little capronic acid.

20 c.c. $N/2$-acid. 20 c.c. $N/2$-amide.
$\theta = 63{\cdot}2°$. $Q = 11{\cdot}09$.
Initial concentration $= N/4$.

t.	σ.	$C \times 10^5$.	$C' \times 10^5$.	K.
11·50	0·1305	24·23	22·02	12·20
16·00	0·1293	23·95	21·80	12·18
25·50	0·1273	23·35	21·22	12·20
34·50	0·1258	22·83	20·75	12·19
51·50	0·1225	21·88	19·87	12·21
56·25	0·1217	21·63	19·65	12·21
61·00	0·1209	21·39	19·40	12·22
70·08	0·1190	20·94	19·07	12·17
79·50	0·1178	20·48	18·62	12·19
90·00	0·1166	20·00	18·20	12·18
100·25	0·1149	19·56	17·77	12·20
			Mean K =	12·19

$\sigma^0 = 0{\cdot}1330$, $\sigma^{0{\cdot}2} = 0{\cdot}1163$. Range 0 to 20 per cent.

It will be seen that capronamide is much more reactive than valeramide, and is slightly greater in reactivity than butyramide.

Formamide.—Owing to the rapid rate of reaction, somewhat dilute solutions were employed. In the following numbers, t is the time of the reaction to concentration C, and a is the fraction of dissociation of hydrochloric acid under the given conditions.

25 c.c. each of $N/4$-acid and amide.

$\theta = 63·2°$. Initial concentration $= N/8$.

t.	$C \times 10^5$.	$(1/c - 1/c^0)$.	a.	K
0	12·50	0	0·9167	—
8·40	9·375	2666	—	346·2

One standard mixture only was used in this case.

As might have been expected, the constant has a very high value.

At 63·2°, the values for the velocity-constants of the homologous fatty amides examined are as follows:

Formamide	– 346·2	*iso*Butyramide	– 14·88
Acetamide	21·58	Valeramide	3·343
Propionamide	25·67	Capronamide	12·19
n-Butyramide	11·84		

(b) *The Influence of Temperature on the Reactivities of the Amides.*

The temperature-coefficients of reactivity are very large. Acetamide is nearly eight times as reactive at 63° as it is at 42°, about sixteen times as great at 70°, and about thirty-four times more reactive at 80° as at 42°.

In the following experiments the general method was to determine the conductivity at given intervals of time of a mixture of acid and amide, and then to repeat the process, using a synthetical mixture of amide, acid, and products, which represented the condition when 25 per cent. of the reaction had taken place. Generally 15 c.c. each of hydrochloric acid and amide and 5 c.c. each of organic acid and ammonium chloride, all of equivalent strengths, were used.

By extrapolation of the resistance-time curve of the second experiment, the conductivity of the mixture when 25 per cent. of the reaction had taken place was determined. Comparison with the curve of the original reaction gave the time of reaction to this stage of the decomposition.

If C = concentration of amide at time t.

aC = ionic concentration of hydrochloric acid at time t.

The velocity of reaction is given by

$$-\frac{dc}{dt} = aKC^2,$$

$$\text{whence } aKt = -\int \frac{dc}{c^2} + \text{constant}.$$

If C_0 is the initial concentration of the amide,

$$K = \frac{1}{at}\left(\frac{1}{c} - \frac{1}{c^0}\right)$$

This result is dependent on the assumption that the concentration of the hydrogen ions is proportional to the molecular concentration of the hydrochloric acid or amide. This is nearly true for the range examined, the maximum error observed for 30 per cent. of the reaction being 0·8 per cent.

Reference to the curves in Fig. 2 will illustrate this point. The ionic concentration is nearly a linear function of the molecular concentration, and within the limits stated will be seen to be practically proportional to it.

The degrees of dissociation of hydrochloric acid and ammonium chloride in solution of various dilutions at 63·2° were determined by the author. The values for hydrochloric acid at other temperatures were calculated from Krannhals's numbers (*Zeitsch. physikal. Chem.*, 1890, 5, 250). There is apparently a slight error in these data, since the degree of dissociation does not vary in a regular manner with the temperature. It was noticed that unless unplatinised electrodes were used for hydrochloric acid at high dilution at 63·2°, no definite result could be obtained owing to the gradual decrease of the conductivity with time. The error caused on the "constants" in this section of the paper by using these values is probably not greater than ±1 per cent.

In the following tables:

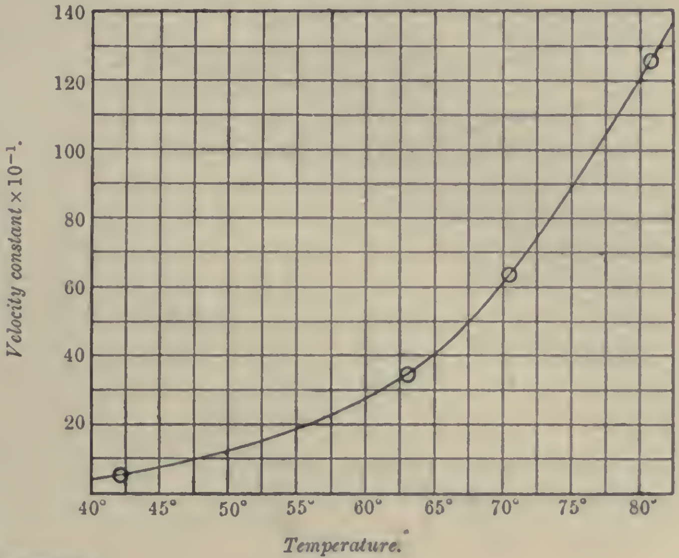
θ = temperature;
t = time of reaction in minutes;
C = concentration of amide in gram-equivalents per c.c.;
a = fraction of dissociation of hydrochloric acid;
K = velocity-constant.

Formamide:

θ.	t.	$C \times 10^5$.	$(1/c - 1/c^0)$.	a.	K.
42·10	0	25	0	0·8935	52·07
	28·65	18·75	1333	—	—
Initial concentration = $N/4$.					
63·20	—	—	—	—	346·2
	—	—	—	—	—
v. supra.					
70·30	0	3·125	0	95·79	635·1
	17·54	2·344	106·7	—	—
Initial concentration = $N/32$.					
80·70	0	3·125	0	95·90	1259
	8·84	2·344	106·7	—	—
Initial concentration = $N/32$.					

These results show the large temperature-coefficients of reactivity. In the curve below, which is characteristic, the temperature-variation of the velocity constant is shown.

FIG. 4.



Acetamide :

θ.	t.	$C \times 10^5$.	$(1/c - 1/c_0)$.	a.	K.
42·10	0	100	0	78·62	2·647
	160	75	333	—	—
		Initial concentration = N.			
63·20	—	—	—	—	21·58
	—	—	—	—	—
		v. supra.			
70·30	0	25	0	89·43	40·96
	36·40	18·75	1333	—	—
		Initial concentration = $N/4$.			
80·70	0	25	0	89·51	89·06
	16·71	18·75	1333	—	—
		Initial concentration = $N/4$.			

Propionamide :

θ.	t.	$C \times 10^5$.	$(1/c - 1/c_0)$.	a.	K.
42·10	—	100	—	78·62	3·542
	44·90	88·88	125	—	—
		Initial concentration = N.			
63·20	—	—	—	—	25·67
	—	—	—	—	—
		v. supra.			

Propionamide :

θ.	t.	$C\times10^5$.	$(1/c-1/c_0)$.	α.	K.
70·30	0	25	0	0·8943	55·22
	27·00	18·75	1333	—	—
Initial concentration $= N/4$.					
80·70	0	25	0	0·8951	111·4
	13·37	18·75	1333	—	—
Initial concentration $= N/4$.					

It will be seen that in every case propionamide is more reactive than acetamide.

Butyramide :

θ.	t.	$C\times10^5$.	$(1/c-1/c_0)$.	α.	K.
42·40	0	75	0	0·8210	1·818
	112·6	66·66	168	—	—
63·20	0	75	0	0·8120	11·84
	18·00	66·66	168	—	—
Initial concentration $= \frac{3}{4}N$.					
70·30	0	25	0	0·8943	24·64
	60·50	18·75	1333	—	—
Initial concentration $= N/4$.					
80·70	0	25	0	0·8951	58·30
	25·55	18·75	1333	—	—
Initial concentration $= N/4$.					

iso*Butyramide :*

θ.	t.	$C\times10^5$.	$(1/c-1/c_0)$.	α.	K.
42·10	0	75	0	0·8210	2·118
	96·61	66·66	168	—	—
Initial concentration $= \frac{3}{4}N$.					
63·20	—	—	—	—	14·88
	—	—	—	—	—
v. supra.					
70·30	0	25	0	0·8943	28·13
	53·0	18·75	1333	—	—
Initial concentration $= N/4$.					
80·70	0	25	0	0·8951	62·86
	23·70	18·75	1333	—	—
Initial concentration $= N/4$.					

Valeramide :

θ.	t.	$C\times10^5$.	$(1/c-1/c_0)$.	α.	K.
63·20	—	—	—	—	3·343
	—	—	—	—	—
v. supra.					

Valeramide:

θ.	t.	$C \times 10^5$.	$(1/c - 1/c_0)$.	a.	K.
70·30	0	25	0	0·8943	6·111
	244	18·75	1333	—	—

Initial concentration $= N/4$.

θ.	t.	$C \times 10^5$.	$(1/c - 1/c_0)$.	a.	K.
80·70	0	25	0	0·8951	15·12
	98·52	18·75	1333	—	—

Initial concentration $= N/4$.

Capronamide:

θ.	t.	$C \times 10^5$.	$(1/c - 1/c_0)$.	a.	K.
63·20	—	—	—	—	12·19
	—	—	—	—	—

v. supra.

θ.	t.	$C \times 10^5$.	$(1/c - 1/c_0)$.	a.	K.
70·30	0	25	0	0·8943	26·73
	55·80	18·75	1333	—	—

Initial concentration $= N/4$.

θ.	t.	$C \times 10^5$.	$(1/c - 1/c_0)$.	a.	K.
80·70	0	25	0	0·8951	63·00
	23·65	18·75	1333	—	—

Initial concentration $= N/4$.

The order of the reactivities of the amides except for capronamide at 80·7° is the same for all temperatures within the range examined. This order is, formamide, propionamide, acetamide, *iso*butyramide, capronamide, butyramide, valeramide.

At first sight the above results do not exhibit any simple relation. There is a general decrease of reactivity with increasing molecular weight; but there are some remarkable points about the values for the individual members. The position of propionamide is unexpected, and, contrary to expectation, *iso*butyramide is more reactive than butyramide. The value for valeramide is also remarkably small.

By comparison with the corresponding organic acids, it is seen, however, that there is a similar, although less marked, variation of the dissociation-constants of these acids.

Acid.	$K' \times 10^6$.	Amide.	K at 63·2°.
Formic	214·0	Formamide	346·2
Acetic	18·0	Acetamide	21·01
Propionic	13·4	Propionamide	25·67
Butyric	14·9	Butyramide	11·84
*iso*Butyric	14·4	*iso*Butyramide	14·88
Valeric	16·1	Valeramide	3·34
Capronic	14·5	Capronamide	12·19

In the above, K' and K are respectively the dissociation-constants of the acids and the velocity-constants of the amides. Except in the case of formamide, on comparing successive members, a decrease in the strength of the acid corresponds to an increase in the velocity-constant of the amide; for example, butyric acid is a stronger acid than *iso*-

butyric acid. Hence *iso*butyramide is more reactive than butyramide. A small change in electrochemical character, however, produces a large change in reactivity. This is in accordance with our knowledge of the general susceptibility of reactivity to small variations of condition, internal or external.

The relation between reactivity at constant temperature and molecular weight is not a simple function. There is evidently some influence at work which does not depend on the constitution in the usual manner. This influence is probably association. If association does take place, non-ionised molecules must result; and, moreover, since the velocity-constant is independent of the volume of the system, the equilibrium formula relating to the simple and associated molecules must be of the first order. This precludes association of amide molecules *inter se*, and makes it probable that the amide associates with the solvent, with the production of hydrated non-ionisable molecules:

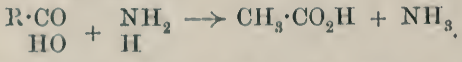
$$CH_3\cdot CO\cdot NH_2 + H_2O \rightleftarrows CH_3\cdot CO\cdot NH_3\cdot OH.$$

The velocity of reaction thus depends on the ratio of the concentrations of the two forms and also on their relative rates of reaction with hydrochloric acid. Increase of molecular weight would tend to reduce the "mobility" of the amide molecules and thus the reactivity. On the other hand, the variation of the relative concentration of the hydrated form with increase of molecular weight would probably run parallel with the strengths of the corresponding acids, an increase of acidic power in the acid corresponding to a decrease of associative power in the amide.

The direct steric effect in the case of *iso*butyramide and butyramide is masked, probably owing to the high mobility and relative smallness of the hydrogen ion.

The exact mechanism of the reaction is not easy of explanation. The marked accelerative power of the hydrogen ion in reactions of hydrolysis is very probably connected with its high mobility.

Representing the amide as the simple molecule, hydrolysis takes place in the following manner:



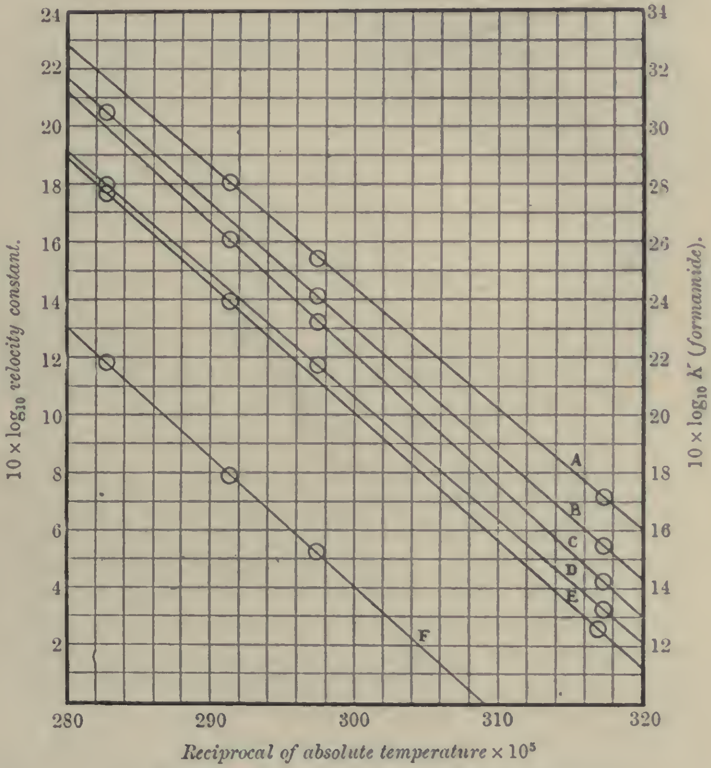
$$\begin{matrix}R\cdot CO\\ HO\end{matrix} + \begin{matrix}NH_2\\ H\end{matrix} \longrightarrow CH_3\cdot CO_2H + NH_3.$$

The bombardment of the molecule by the rapidly moving hydrogen ions facilitates the decomposition into two parts, and the latter combine with the disintegrated water molecules simultaneously produced. Naturally the stronger the organic acid *cæteris paribus*, the more stable is the amide molecule in the presence of hydrochloric acid. Although it is at present an open question whether the action of alkali is to be considered one of hydrolysis or of direct "saponification," it is significant that the hydroxyl ion has also a large mobility, being next to hydrogen in this respect.

Consideration of the temperature variation of the velocity-constants brings out some points of interest.

When $\log K$ and the reciprocal of the absolute temperature $1/T$ are plotted together, the graphs are found to be straight lines. These are shown in the diagram below:

FIG. 5.



A. Formamide.
B. Propionamide.
C. Acetamide.
D. *iso*Butyramide.
E. Butyramide.
F. Valeramide.

The relations are accurately represented by the general formula,

$$\log K = \log K_0 + B\left(\frac{1}{T^0} - \frac{1}{T}\right),$$

where K_0 is the velocity-constant at a standard temperature T^0. If T^0 is put equal to infinity, then,

$$\log K = C - \frac{B}{T},$$

where $\log^{-1}C$ is a constant which would represent the reactivity under the hypothetical condition of infinite temperature if the relation were true for all temperatures.

The former formula is to be preferred for practical purposes. Below are the values of the constants for the various amides:

	$\log K_0$.	B.	$1/T^0$.	C.	$\log^{-1}C \times 10^{-13}$.
Formamide	1·7166	4182	0·003173	14·987	97·0
Acetamide............	0·4227	4542	,,	14·843	69·6
Propionamide	0·5492	4335	,,	14·309	20·3
Butyramide	0·2596	4405	0·003170	14·230	17·0
*iso*Butyramide	0·3259	4260	0·003173	13·846	7·0
Valeramide	0·5241	4395	0·002974	13·594	3·9

Common logarithms are used throughout. The degree of accuracy obtained by using the first formula is shown by reference to the following results for 84·1°:

	K (from curve).	K (calc.).
Formamide	1884·0	1890·0
Acetamide	131·2	131·1
Propionamide	146·2	146·6
Butyramide	77·61	77·55
*iso*Butyramide	81·83	82·20
Valeramide	19·45	19·44

Owing, apparently, to the separation of the acid during hydrolysis, the results for capronamide do not follow the above simple temperature relation, and therefore the calculation of the "constants" is not possible in this case.

The values of $\log^{-1}C$ given above are independent of temperature and are characteristic of the substance.

It will be noticed that these factors decrease with increasing molecular weight. Moreover, here the factor for *iso*butyramide is less than for butyramide. The influence of a small error in B however, is greatly magnified in the calculation of $\log^{-1}C$, and this fact detracts from the quantitative value of these factors. Better results are obtained by evaluating the velocity-constants at "corresponding" temperatures, using the term "corresponding" in a wide sense (compare Thorpe and Rodger, *Phil. Trans.*, 1894, **185**, *A*, 397).

"Corresponding" temperatures for the different amides as here defined are such that the differential coefficients of the reactivity-temperature curves at these temperatures are equal.

The temperature relation can be expressed in the form:

$$K = A\epsilon^{-nB/T}$$

where A and B are constants characteristic of each amide, and n is the logarithm modulus. On differentiation,

$$\frac{dK}{dt} = \frac{nKB}{T^2} = n\phi.$$

Then when ϕ is the same for all the amides, they are under corresponding conditions. The relation between $\log_{10}\phi$ and $1/T$ is nearly a linear function, and putting $\log_{10}\phi = x$ and $1/T = y$, can be accurately expressed by,

$$y = a + bx + cx^2.$$

The constants in this equation for the amides considered are:

	a.	*b.*	*c.*
Formamide	$0{\cdot}0_2 3259$	$-0{\cdot}0_3 2548$	$-0{\cdot}0_6 965$
Acetamide	$0{\cdot}0_2 2957$	$0{\cdot}0_3 2371$	$0{\cdot}0_6 617$
Propionamide	$0{\cdot}0_2 2972$	$0{\cdot}0_3 2475$	$0{\cdot}0_6 711$
Butyramide	$0{\cdot}0_2 2904$	$0{\cdot}0_3 2436$	$0{\cdot}0_6 699$
*iso*Butyramide	$0{\cdot}0_2 2910$	$0{\cdot}0_3 2525$	$0{\cdot}0_6 787$
Valeramide	$0{\cdot}0_2 2757$	$0{\cdot}0_3 2451$	$0{\cdot}0_6 733$

Assigning values $x = 0$ and $x = 1$, we obtain for the reactivities under these two sets of corresponding conditions the following numbers:

	$\log_{10}\phi = 0.$			$\log_{10}\phi = 1.$		
	T.	*K.*	*K*¹.	*T.*	*K.*	*K*¹.
Formamide	307·7	22·54	10·00	333·1	265·5	10·00
Acetamide	338·2	25·34	11·23	367·6	302·7	11·40
Propionamide	336·5	26·15	11·59	367·1	310·7	11·71
Butyramide	355·2	26·91	11·93	376·0	321·2	12·10
*iso*Butyramide	343·6	27·67	12·28	376·4	332·0	12·51
Valeramide	362·8	30·00	13·30	398·2	361·4	13·62

In the last column, K^1 represents the relative activity in each case when formamide is taken equal to 10. This ratio is practically constant for each amide at all temperatures over the range considered. It will be seen that the "relative reactivity" at corresponding temperatures gradually increases with rise of molecular weight.

From the velocity-constants of the amides it is possible to calculate approximately their stability in aqueous solution. The time in years for a 1 per cent. decomposition is given by:

$$t = \frac{\mu\infty}{K\sigma(r+1)} \log_e \frac{100}{99} / 60 \times 24 \times 365.$$

where σ = specific conductivity of water;

$\mu\infty$ = molecular conductivity of water at infinite dilution.

r = ratio of hydrolytic power of hydroxion and hydrion.

At a temperature of 15°, taking $K = 0{\cdot}107$ for acetamide, $\sigma = 2 \times 10^{-6}$, and $r = 2{\cdot}5$, t is about eleven years.

The specific conductivity of a normal solution of acetamide at the laboratory temperature changed in four months by 25×10^{-6} mhos. Taking μ_∞ for ammonium acetate = 98, this gives a rate of decomposition of 1 per cent. in about twelve years, which is in fair agreement with the above number.

In conclusion, the author wishes to express his thanks to Professor Collie for kindly supervising the work, and also his appreciation of suggestions offered by him and by Dr. F. G. Donnan.

CHEMICAL DEPARTMENT,
S.W. POLYTECHNIC,
CHELSEA, S.W.

LX.—*Interaction of Alkali Starch and Carbon Disulphide. Xanthogenic Esters of Starch.*

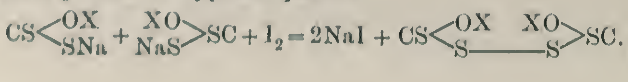
By CHARLES FREDERIC CROSS, EDWARD JOHN BEVAN, and JOHN FREDERIC BRIGGS.

THE xanthogenic esters of cellulose, which have been described in a series of communications (Trans., 1893, **63**, 837; *Ber.*, 1893, **26**, 1090, *ibid.*, 1901, **34**, 1513; *Researches on Cellulose*, I. and II.) revert to cellulose progressively over a period more or less prolonged, depending on temperature and other conditions, and the stages of these reverse decompositions have been studied as characteristic more especially of the aqueous solutions of the product (viscose).

From the many analogies existing between starch and cellulose it has been *a priori* evident that the corresponding xanthogenic esters of the former would be produced under analogous conditions of reaction; but to control these conditions so as to obtain the intimate mixture of the necessary reagents, namely, starch, alkali hydroxide, water, and carbon disulphide, has been a matter of some difficulty.

By the particular device of moistening the starch with carbon disulphide, and then adding sodium hydroxide in 15—20 per cent. solution, a liquid mixture is obtained, which, however, rapidly changes to a swollen but non-coherent mass; the carbon disulphide is held as an emulsion in the semi-solid alkali-starch hydroxide, and under these conditions the reaction proceeds similarly to the cellulose reaction and is complete in two to four hours.

The product is now soluble in cold water and is fully converted into the new derivative. It is accompanied, as in the case of the cellulose reaction, by the inevitable by-products of reaction, chiefly sodium trisulphocarbonate, which gives it a yellow colour. The purified product can be obtained by treating with dehydrating agents, such as alcohol. On adding acetic acid the by-products are decomposed, the sodium xanthogenate resisting the action of the acid as in the case of the cellulose; it now reacts with iodine in the quantitative proportions corresponding with the typical equation:



$$\mathrm{CS}\!<^{\mathrm{OX}}_{\mathrm{SNa}} + {}^{\mathrm{XO}}_{\mathrm{NaS}}\!>\!\mathrm{SC} + \mathrm{I}_2 = 2\mathrm{NaI} + \mathrm{CS}\!<^{\mathrm{OX}}_{\mathrm{S}}\text{———}{}^{\mathrm{XO}}_{\mathrm{S}}\!>\!\mathrm{SC}.$$

The following experimental results may be cited as typical.

(1) Twenty grams of dry starch were mixed with 12·5 grams of carbon disulphide and then with 42 grams of sodium hydroxide solution (20 per cent.). Under these conditions the incorporation of the reagents together is incomplete, and we found it convenient to use toluene as a diluent.

(2) 21·9 Grams of dry starch were treated with 11 grams of carbon disulphide diluted with 10 grams of toluene, 55 grams of a 20 per cent. solution of sodium hydroxide were now added to the mixture, and the whole stirred during solidification, which was sufficiently retarded for perfect mixture. The reaction was continued for several hours and the mass then diluted to a total weight of 300 grams.

This specimen was analysed on a sequence of days covering a period of two to three weeks, and the numbers (below) established the very close similarity of the starch product with the cellulose analogues (see *Researches on Cellulose*, II, pp. 98—99).

The particular constitutional index of the series is the soda combined with the xanthate residue, which is estimated by titrations based upon the quantitative reaction with iodine above cited.

The necessary correction is applied for the ascertained proportion of iodine consumed by the associated by-products. The method is based upon our communication in *Ber.*, 1901, **34**, 1513.

It may not be superfluous to set out briefly the main points to be noted in the analytical investigation of these colloidal substances.

(1) The ester may be freed from saline by-products by precipitation by a neutral dehydrating agent. When "pure" the alkalimetric and iodometric estimations (of the sodium) give identical results, and the identity is a criterion of "purity."

(2) Sulphur is estimated as $BaSO_4$ after fully oxidising with hypochlorite: the pure compounds give the ratio S : Na = 2 : 1 ; lastly, the pure colloid itself is isolated after decomposition by a mineral acid, purified, dried, and weighed.

On a series of determinations it is convenient to make observations on the crude solution. The details of the analytical method applicable to this have been carefully worked out by our collaborator, Monsieur L. Naudin.

The iodometric estimation is carried out under a condition of high dilution, 0·25 gram of the colloid per 1000 c.c. Comparative titrations in separate portions, *A* after adding acetic acid, *B* after adding sulphuric acid, afford the necessary data.

In the series of observations of the specimen of the starch derivative the following numbers were obtained:

Age of preparation.	Soda combined as XOCSSNa, represented as NaOH per cent. of original starch.
1 day	19·2
5 days	10·5
6 ,,	10·3
7 ,,	9·0
16 ,,	5·2

The original reaction takes place in the approximate stoichiometrical ratio $C_6H_{10}O_5 : CS_2 : NaOH$.

It is interesting to note that starch undergoes only a slight incidental hydrolysis in soluble derivatives under the conditions of the reaction, and the proportions precipitated by iodine as dixanthogenide closely correspond with the percentage calculated from the quantity of starch originally taken.

The investigation of this series of derivatives will be found to throw some light on a point which is obscure in the case of cellulose by reason of the difficulty of determining as between the cellulose (hydrate) and cellulose xanthogenic derivatives containing only a fractional quantity of the CSS residues.

Taking the colour reaction of starch with iodine as the basis of observations, we find that no starch can be detected *as starch* throughout the series of stages of spontaneous decomposition and "reversion."

Thus, after acidifying with acetic acid and adding excess of iodine no colour is developed, but the addition of mineral acid, by immediate decomposition of the xanthogenate, develops the characteristic iodine reaction.

A graphic representation of the stages of reversion would be marked by an asymptotic approach to the line of starch, as of cellulose in the case of viscose. In either case there is a remarkable persistence of fractional residues of the characteristic CSSNa groups, influencing one complex and differentiating its reactions from those of starch.

It might be urged as regards the quantitative relations that these residues are the reciprocal measure of the molecule or the reacting unit of the carbohydrate, and that this is of definitely large magnitude. The alternative view is that the reacting unit is a system, homogeneous as regards a particular chemical function, although heterogeneous in actual constitution. This appears to be the simplest way of stating the experimental facts in accordance with the observations that at no stage of the reversion are the products a mixture of starch and its thiocarbonic esters.

The investigations of these products have been carried out in the Laboratory of the Société Française de la Viscose. We wish to express our obligations to this Company and to their Chemist Director, Monsieur L. Naudin.

ANNUAL GENERAL MEETING,

MARCH 22ND, 1907.

Professor R. MELDOLA, F.R.S., in the Chair.

Dr. G. D. Lander and Dr. J. F. Thorpe were appointed scrutators, and the Ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society during the past twelve months. The adoption of the Report of the Council was proposed by Prof. J. B. Harrison, seconded by Prof. W. Jackson Pope, and carried unanimously.

REPORT OF THE COUNCIL.

THE Council have the satisfaction of being able to report the continued prosperity of the Society and that, measured by the number of papers read and the number of Fellows on the list, there has been greater activity than in any previous year.

On the 31st December, 1905, the number of Fellows was 2,785. During 1906, 172 Fellows were elected and 2 reinstated, thus making a gross total of 2,959. The Society has lost 24 Fellows by death; 24 have resigned, the elections of 5 have become void; 39 have been removed for non-payment of Annual Subscriptions, and 7 Life Compounders, whose addresses could not be found, have been removed.

The total number of Fellows, therefore, on the 31st December, 1906, was 2,860, showing an increase of 75 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are :

W. H. Chandler (1872).
F. J. Claudet (1852).
T. S. Davis (1876).
W. H. Edwards (1902).
M. H. Foye (1884).
C. H. B. Hambly (1859).
J. G. Hepburn (1853).
J. S. C. Heywood (1848).
G. H. Hurst (1885).
F. M. Lyte (1859).
C. W. Marsh (1881).
E. H. Miller (1897).
W. J. Orsman (1884).
B. Phillips (1889).
J. E. Pitman (1906).
T. Royle (1862).
F. Smith (1890).
T. D. Smith (1898).
H. J. P. Sprengel (1864).
W. S. Squire (1858).
J. A. Storey (1891).
C. Tookey (1855).
T. B. Tyson (1885).
A. Walker, Maj-Gen. (1868).

The following Fellows have resigned :

G. D. Atkinson.
J. Bateman.
W. C. T. Beasley.
Sir B. V. S. Brodie, Bt.
C. H. Burge.
J. M. Campbell.
H. E. Ellis.
J. C. Fell.
P. Haigh.
S. M. Haigh.
W. Harris.
E. Hughes.
R. B. Lee.
H. L. Leech.
H. P. Lewis.
W. C. Mackenzie.
A. S. Mayfield.
J. B. Moody.
J. W. Sandford.
G. T. S. Sichel.
W. H. Sodeau.
R. C. Styles.
G. E. Tomlins.
P. J. Vinter.

The names of the Life Compounders whose address cannot be found, and who have been removed therefore by the Council are :

G. Crampton (1875).
J. Danson (1850).
A. A. Ferreira (1864).
A. W. Gillman (1865).
J. Hadkinson (1878).
F. E. Harman (1874).
James Millar (1848).

The number of the Fellows who were elected in the early part of the last century has been still further diminished by the death of Mr. F. J. Claudet, elected on 16th February, 1852; Mr. J. G. Hepburn, elected on 21st February, 1853, and of Mr. J. S. C. Heywood, who was elected on 3rd April, 1848.

The number of Honorary and Foreign Members at the close of 1905 was 34. No elections have been held during 1906, but the Society has to mourn the loss of Dr. Fedor Beilstein, who was elected 1st February, 1883, and who died on 19th October, 1906. The number of Honorary and Foreign Members at 31st December, 1906, was therefore 33.

Since the close of 1906, the Society has lost by death three more of its Honorary and Foreign Members, namely, Prof. Dr. D. I. Mendeléeff, (on the 2nd February), Prof. Dr. Nicolai Menschutkin (on the 4th February), and Prof. Henri Moissan (on the 20th February).

During the year 1906, 236 scientific communications have been made to the Society, 176 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of Transactions for 1906 contains 1,943 pages, of which 1,890 are occupied by 186 memoirs, the remaining 53 pages being devoted to the Cleve Memorial Lecture, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 184 memoirs, which occupy 1,818 pages.

The Journal for 1906 contains also 4,541 abstracts of papers published mainly in foreign journals, which extend to 1,912 pages, whilst the abstracts for 1905 numbered 4,356, and occupied 1,828 pages.

The abstracts for 1906 may be classified as follows:

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	1,000	1,745
Part II.		
General and Physical Chemistry		651
Inorganic Chemistry		559
Mineralogical Chemistry		128
Physiological Chemistry		486
Chemistry of Vegetable Physiology and Agriculture		343
Analytical Chemistry		629
	912	2,796
Total in Parts I. and II.	1,912	4,541

Among the first acts of the Council elected in March, 1906, was the appointment of a Finance Committee, and it was decided also that the names of the Members, together with those of the House, Library, Publication, and Research Fund Committees, should be read from the Chair at the Ordinary Meeting next after the Meeting of Council at which the Committees are formed.

In the previous session, and on a second occasion during the present one, the desirability of reading the minutes at an Ordinary Meeting has been called in question; for the guidance of Chairmen on this point it has been resolved that henceforth the minutes must be read as long as the present Bye-Laws remain in force.

The practice of holding the Ordinary Meetings of the Society on the first and third Thursdays of the month, reversion to which was announced in the last Annual Report, appears justified by the average attendance of Fellows, which has been well maintained. In order to relieve the pressure of business which has been usual at the first and last Meetings of the Session, it was decided to hold two extra Meetings, in October and July respectively.

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote Chemical Science by Research, was made, on the recommendation of the Research Fund Committee, to Prof. Walter Noel Hartley, F.R.S., in recognition of his spectrochemical investigations. The medal was presented on October 18th, 1906.

On the occasion of the International Celebration marking the Fiftieth Anniversary of the Foundation of the Coal Tar Colour Industry, an address of congratulation to Sir William Henry Perkin, F.R.S., was presented on behalf of the Society by the President. In accordance with the resolution of the public meeting at which the commemoration was inaugurated, a marble bust of Sir William Perkin, executed by Mr. F. W. Pomeroy, A.R.A., has been presented to the Society by the Committee administering the Fund subscribed in support of the celebration.

The Society has also received a Berzelius medal cast in selenium, presented by Mr. John Spiller, and Prof. J. M. Thomson, F.R.S., has presented an aqua-tint engraving of Dr. Thomas Thomson, F.R.S., Regius Professor of Chemistry in the University of Glasgow from 1818 to 1852.

During the vacation of 1906 an address was presented to the University of Aberdeen at the celebration of its fourth centenary, which took place in September. The congratulations of the Society were offered also to the distinguished Honorary and Foreign member, Professor Adolph Lieben, on the occasion of his seventieth birthday and fiftieth anniversary of his doctorate.

The desirability of applying for a supplemental Charter with a view to removing existing restrictions in regard to nationality and sex as affecting election to the Fellowship of the Society has been carefully considered by the Council. After receiving the report of a Special Committee consisting of Mr. Phipson Beale, Mr. Bousfield, Dr. Horace Brown, Dr. Moody, Professor Emerson Reynolds, Dr. T. E. Thorpe, Professor W. A. Tilden, and the Officers, the Council resolved that for the guidance of Chairmen, only those Fellows who are British subjects can vote at meetings or be eligible for offices, and that the matter be made clear by adding to the gloss on the Charter, after the first paragraph, the words "but British subjects who are Fellows can alone exercise corporate rights, or be eligible for office."

The Council has resolved that, following the ordinary index of the Transactions, there shall appear a list of new compounds described in the original communications, tabulated according to the Richter system.

The alchemical and early chemical works presented to the Library by Sir Henry E. Roscoe have been catalogued (Proc., 1906, **22**, 209—233) and the volumes placed in a special book-case.

The number of books borrowed from the Library during 1906 was 1,126, as against 1,108 in the previous year. The additions to the Library comprise: (*a*) a collection of 136 alchemical and other books presented by Sir Henry E. Roscoe; (*b*) 121 books, of which 64 were presented, 385 volumes of periodicals, and 32 pamphlets, as against 165 books, 324 volumes of periodicals, and 48 pamphlets last year.

In January last the Council decided that during the remainder of the present Session the Library shall be kept open for the use of Fellows every Thursday from 10 a.m. until 9 p.m., except on those evenings on which the Society meets, when it will remain open until 10.30 p.m.

The annual income of the Research Fund from its investments is £219 17*s*. 0*d*., and from this, grants amounting to £210, as well as the Longstaff Honorarium and Medal, had to be paid. That this should be not only possible, but that there should also be an excess of income over expenditure of £26 13*s*. 11*d*. for the year, is due to the amount of £38 6*s*. 11*d*. having been returned from grants made in previous years. In the Transactions for 1906 there are 31 papers contributed by authors to whom grants had been made from the Research Fund.

The Treasurer has great pleasure in recording that in February of the present year the Society received a further munificent donation of £1000 to the Research Fund from the Worshipful Company of Goldsmiths. The income accruing from this donation will, in accordance with the expressed wish of the donors, be devoted especially to the encouragement of research in metallurgy and inorganic chemistry.

The financial transactions of the Society for the past year have been very satisfactory and show a substantial surplus. The total income of the Society for 1906 is £7121 8*s*. 11*d*., being an increase of £327 14*s*. 11*d*. over that for 1905 (£6793 14*s*. 0*d*.), in spite of the fact that the amount received on account of Life Composition Fees has fallen from £360 to £268, a decrease of £92. The increase in income is mainly composed of the following three items: (1) admission fees, £120; (2) annual subscriptions, £138 18*s*. 0*d*., and (3) sale of publications, £120 6*s.* 3*d.* Whilst the income has notably increased, the expenditure has fallen much more considerably and is £718 19*s.* 8*d.* less than last year, so that instead of a deficit of £305 1*s.* 5*d.* on the year's working there is a surplus of £741 13*s.* 2*d.*, a difference in all of £1046 14*s.* 7*d.* This is due very largely to having no expenses of any kind to meet on account of the Collective Index, which last year alone cost the Society £778 10*s.* 5*d.*, but it must not be thought that nothing is being done towards the preparation of the next volume, because the card indexes now made by Mrs. Dougal for each Annual Index will, with comparatively little expense and labour, be blended together and thus utilised for the preparation of Vol. V. of the Collective Index, which will cover the period 1903—1912.

The cost of the *Journal*, the *Proceedings*, and the *Annual Reports* all show increased expenditure, amounting to £71 7*s.* 6*d.*, £40 6*s.*, and £68 10*s.* 7*d.* respectively. It is very satisfactory to notice that although the Transactions and Abstracts show an increase of over 200 pages and contain several lengthy, as well as important and expensive, papers, the increase in cost should be so small. In this connexion the Treasurer has to thank Professor Pope and Mr. Barlow for supplying all the blocks required to illustrate their paper published in the November issue of the *Journal.* The increased cost of the Proceedings is due in part to the issue of two additional numbers corresponding to the two extra Meetings of the Society in July and in October, and in part also to the printing of the catalogue, compiled with great care by the Librarian, of the collection of alchemical works above referred to which the Society owes to the generosity of Sir H. E. Roscoe, and which are now properly housed in the Library.

The balance sheet also shows that a small legacy of £33 12*s.* 3*d.* has been received under the will of the late Mr. Henry Dircks, and is a residue of the estate from which almost exactly thirty years ago the Society received £840 5*s.*

The TREASURER gave a statement as to the Society's Income and Expenditure during the year 1906, and proposed a vote of thanks to the Auditors, which was seconded by Dr. W. R. E. Hodgkinson and carried unanimously. Acknowledgment was made by Mr. E. Grant Hooper.

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31ST DECEMBER, 1906.

Liabilities.

	£	s.	d.	£	s.	d.
To Subscriptions received in advance, 1907	237	0	0			
,, ,, ,, ,, 1908	4	0	0	241	0	0
,, Cash received on Account of Annual Report Vol. 3 (not published)				19	4	0
,, Sundry Creditors				859	19	7
,, Research Fund :—						
As per last Balance Sheet	6790	19	7			
Add Excess of Income over Expenditure for the year	26	13	11	6817	13	6
,, Chemical Society :—						
As per last Balance Sheet...	18394	0	1			
Add Excess of Income over Expenditure for the year	741	13	2	19135	13	3
				£27073	10	4

Assets.

	£	s.	d.	£	s.	d.
By Investments (value when acquired):—						
£1050 London and North Western Railway 3 per cent. Debenture Stock	839	12	0			
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212	8	6			
£1520 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock	1650	0	0			
£1400 India 2½ per cent. Stock	1316	1	0			
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0			
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5			
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0			
£1500 Transvaal 3 per cent. Guaranteed Stock ...	1460	13	6	19264	0	5
(Estimated present value of Investments, £17712 16*s*. 10*d*.)						
,, Library, Furniture, Stock of Publications, &c. (not valued)						
,, Sundry Debtors :—						
Society of Public Analysts	12	1	6			
Advertising Agents	44	2	4			
Messrs. Gurney & Jackson	467	11	6			
Telephone Deposit	1	0	0	524	15	4
,, Subscriptions in Arrear, £434. Estimated to realise...				260	0	0
,, Insurance paid in advance				23	19	11
,, Cash at Bank Deposit Account	250	0	0			
Less Overdraft on Current Account	72	6	9			
	177	13	3			
,, ,, in hand	5	7	11	183	1	2
,, Research Fund :—						
Investments (value when acquired):						
£1000 North British 4 per cent. No. 1 Preference Stock	1010	0	0			
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0			
£1084 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11			
	6647	13	11			
(Estimated present value of Research Fund Investments, £6434 10*s*. 5*d*.)						
Cash at Bank	169	19	7	6817	13	6
				£27 73	10	4

INCOME AND EXPENDITURE ACCOUNT

Income.

		£ s. *d.*	£ s. *d.*
To Life Compositions			268 0 0
,, Admission Fees			712 0 0
,, Annual Subscriptions—			
Received in advance, on account of 1906		207 18 0	
,, during 1906 on account of 1906		3973 0 0	
,, ,, ,, ,, 1905		244 0 0	
,, ,, ,, ,, 1904		10 0 0	
		4434 18 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet		250 0 0	
		4184 18 0	
Add Arrears at date: 1906 £410, 1905 £24, estimated to realise as per Balance Sheet		260 0 0	
			4444 18 0
,, Investments :—			
Dividends on £6,730 Metropolitan Consolidated 3½ per cent. Stock ...		223 15 8	
,, £1,050 London and North Western Railway 3 per cent. Debenture Stock		29 18 6	
,, £1 520 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock ...		43 6 8	
,, £1,400 India 2½ per cent. Stock		33 5 0	
,, £2,400 Bristol Corporation 2½ per cent. Debenture Stock		57 0 0	
,, £4,341 Midland Railway 2½ per cent. Preference Stock		103 2 0	
,, £1,200 Leeds Corporation 3 per cent. Stock		34 4 0	
,, £1,500 Transvaal 3 per cent. Guaranteed Stock		42 15 0	
Income Tax Recovered		29 17 0	
Interest on Deposit Account		21 15 5	
			618 19 3
Publications :—			
Sales :			
Journals		849 0 8	
Proceedings		20 6 9	
General Index		67 1 9	
Memorial Lectures		10 12 3	
Library Catalogue		2 9 9	
Atomic Weight Tables		5 4	
Jubilee Volume		5 6	
Annual Report on the Progress of Chemistry. Vol. I		36 6 6	
,, ,, Vol. II		93 11 6	
		1080 0 0	
Less Publishers' Commission		102 4 5	
		977 15 7	
Proceeds of Advertisements in Journal...	£51 18 6		
Less Commission	7 15 8		
		44 2 10	
			1021 18 5
,, Subscriptions from other Societies :—			
Society of Chemical Industry		9 9 0	
Society of Public Analysts		12 1 6	
District Agriculturists' Analysts Association		10 6	
			22 1 0
,, Henry Dirck's Bequest			33 12 3
			£7121 8 11

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

W. B. KEEN,
Chartered Accountant.

6th March, 1907.

FOR THE YEAR ENDED 31ST DECEMBER, 1906.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal and Proceedings:—						
Salary of Editor	300	0	0			
Salary of Sub-Editor	200	0	0			
Salary of Assistant Sub-Editor	60	0	0			
Salary of Indexer	80	0	0			
Editorial Postages, &c.	23	12	9			
Editorial Assistance	15	10	0			
Abstractors' Fees	453	11	6			
Printing of Journal	2338	6	8			
Printing of Advertisements	26	1	0			
Printing of Wrappers	119	1	4			
Distribution of Journal	489	15	8			
Authors' Copies	137	7	9			
Insurance of Stock at Clay's	10	3	0			
				4253	9	8
Printing of Proceedings	224	17	1			
Distribution of Proceedings	67	1	3			
				291	18	4
,, Annual Report on the Progress of Chemistry				514	10	1
,, Purchase of back numbers of Journal				22	11	8
,, List of Fellows				79	5	2
,, Library Expenses:—						
Salary of Librarian	110	0	0			
Books and Periodicals	204	9	6			
Binding	43	9	0			
				357	18	6
,, Indexing for International Catalogue				30	0	0
,, Illuminated Addresses to Sir William Perkin and to the University of Aberdeen				5	4	0
,, Administrative Expenses:—						
Tea Expenses	30	18	0			
Salary of Assistant Secretary	180	0	0			
Salary of Office Assistant	27	12	6			
Wages (Commissionaire, Housekeeper, and Charwoman)	147	16	6			
Pension, Mrs. Hall	30	0	0			
Coal and Lighting	44	2	4			
House Expenses and Repairs	81	3	3			
Insurance	6	17	2			
Accountants' Charges	10	10	0			
Accountants' Commission on Recovery of Income Tax	2	0	10			
Miscellaneous Printing	92	10	7			
Stationery	37	9	1			
Furniture	24	17	2			
Postages	87	15	10			
Miscellaneous Expenses	21	5	1			
				824	18	4
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet				741	13	2
				£7121	8	11

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved— E. GRANT HOOPER,
HY. FORSTER MORLEY,
H. R. LE SUEUR.

RESEARCH FUND INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1906.

Income.	£	s.	d.	£	s.	d.
To Dividends :—						
On £1000 North British Railway 4 per cent. No. 1 Preference Stock	38	0	0			
On £4400 Metropolitan Consolidated 3½ per cent. Stock	146	6	0			
On £1034 Great Western Railway 2½ per cent. Debenture Stock	24	11	2	208	17	2
,, Repayments of Research Grants :—						
A. W. Stewart	1	9	2			
J. F. Thorpe	3	1	0			
J. A. N. Friend		5	0			
H. D. Dakin	4	10	10			
G. D. Lander		7	4			
B. Prentice	9	6	11			
J. Walker	8	5	0			
T. S. Moore	5	0	0			
R. S. Morrell	6	1	8	38	6	11
,, Income Tax Recovered				10	19	10
				£258	3	11

Expenditure.	£	s.	d.	£	s.	d.
By Grants to—						
A. W. Crossley	20	0	0			
A. E. Dunstan	5	0	0			
C. E. Fawsitt	5	0	0			
H. Henstock	10	0	0			
T. M. Lowry	10	0	0			
J. J. Sudborough	10	0	0			
J. F. Thorpe	25	0	0			
W. B. Tuck	5	0	0			
W. Barbour	5	0	0			
H. W. Bywaters	5	0	0			
G. Dean	10	0	0			
K. Fisher	10	0	0			
A. G. Green	10	0	0			
P. Haas	10	0	0			
V. J. Harding	10	0	0			
H. Hartley	5	0	0			
F. M. Perkin	8	0	0			
T. S. Price	5	0	0			
R. Robinson	10	0	0			
J. L. Simonsen	12	0	0			
J. F. Spencer	5	0	0			
A. E. H. Tutton	15	0	0	210	0	0
,, Longstaff Honorarium. Professor W. N. Hartley				20	0	0
,, Cost of Longstaff Medal				1	10	0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet				26	13	11
				£258	3	11

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

6th March, 1907.

Approved— E. GRANT HOOPER,
HY. FORSTER MORLEY,
H. R. LE SUEUR.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Sir William H. Perkin, seconded by Dr. E. Divers, and adopted unanimously; this was acknowledged by Sir William Ramsay.

The President then delivered his address, which will be found on p. 626.

Dr. T. E. Thorpe proposed a vote of thanks to the President coupled with the request that he would allow it to be printed in the Society's *Transactions.* The motion was seconded by Prof. J. Millar Thomson, and carried with acclamation, the President making acknowledgment.

The Scrutators then presented their report to the Chairman, who declared that the following had been duly elected as Officers and Council for the ensuing year:

President: Sir William Ramsay, K.C.B., F.R.S.

Vice-Presidents who have filled the Office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, ScD., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents: J. J. Dobbie, M.A., D.Sc., F.R.S.; Rudolph Messel, Ph.D.; Sir Alexander Pedler, C.I.E., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; A. Smithells, B.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc., Ph.D.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: Edward C. C. Baly; George T. Beilby, F.R.S.; Bernard Dyer, D.Sc.; W. R. E. Hodgkinson, Ph.D.; E. Grant Hooper; H. A. D. Jowett, D.Sc.; H. R. Le Sueur, D.Sc.; F. E. Matthews, Ph.D.; G. T. Moody, D.Sc.; A. G. Perkin, F.R.S.; W. J. Sell, M.A., D.Sc., F.R.S.; John Wade, D.Sc.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, MARCH 22ND, 1907.

By RAPHAEL MELDOLA, F.R.S.

The Position and Prospects of Chemical Research in Great Britain.

THE STATUS OF ORIGINAL RESEARCH.

I HAVE taken for the subject of this year's address a theme which appeals to us all in various ways, and which I propose to discuss under the above heading. According to our Charter we exist as a Society "for the general advancement of Chemical Science." This is tantamount to a declaration that our primary object is the promotion of original research because, although there are many ways of promoting a science, original investigation is unquestionably the most important. Our publications bear testimony to the fact that our Society has well carried out and is still actively promoting the object for which it was founded sixty-six years ago. A critical examination of our publications will further show that the output of original work is, on the whole, increasing both in quality and in quantity. In order to bring out this point our Assistant Secretary, Mr. Carr, has at my request compiled a table dealing with the period from 1895 to 1906 inclusive, and giving under different columns the number of papers contributed to the Transactions and Proceedings, the number of contributing authors, and other useful information. The table itself may be consulted for details,* but just to give an idea of the rate of progress I may state that, in 1895, 109 authors contributed 116 papers to the Transactions and 132 authors contributed 157 abstracts or papers to the Proceedings. In 1906, 183 authors contributed 186 papers to the Transactions and 215 authors contributed 236 abstracts or papers to the Proceedings.

It is impossible to contemplate these figures without coming to the conclusion that a generation of active workers is springing up of which we have every reason to be proud, and in whose keeping we, whose period of activity cannot in the order of nature last very many years, may feel assured that the reputation of our Society will be honourably maintained. Taking advantage of my present position for addressing this newer band of workers, I would venture to point out that the investigations which you are carrying on are of an importance which perhaps even the greatest enthusiasts in your ranks have hardly yet realised. It is not alone the individual discoveries, it is not only your personal contributions to the great edifice of human knowledge, neither is it the practical applications of your discoveries that constitute the supreme importance of this work, the results of which you are giving to the world. We are all labourers in a common cause—the maintenance of the spirit of scientific research—and it is to organisations like this and kindred societies that we look for the preservation and perpetuation of that spirit. Every advance made into the limitless regions of the unknown, whether by a few humble steps or by the flying leap of a great generalisation, must be regarded as a contribution to the common cause. We must take a broad, an imperial view of original research if we desire, as we all do, to influence the public mind. Every discovery emanating from your laboratories not only helps to extend the boundaries of our science but it helps also to uphold the general principle that original research is in itself and by itself the most powerful weapon that has been or ever can be wielded by mankind in struggling with the great problems which nature offers on all sides for solution.

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* See Appendix A, p. 659.

It may appear superfluous for me to sound a pæan on behalf of original research before the Fellows of a Society which ostensibly exists for the very purpose of promoting research. It is, however, unfortunately only too notorious that in this country the general public attitude towards research is either apathetic or else narrowly practical—narrow to the extent of crippling real progress. Although we may all, individually and collectively, realise the importance of our mission, the nation as a whole cannot be said to have given recognition to the principle that the productive activity of the scientific worker is one of the prime factors concerned in all national development, and that the credit of the country in the eyes of the civilised world demands that our rate of progress in the field of scientific discovery should go on increasing from generation to generation. It may be useful, therefore, to take advantage of opportunities such as this to remind the outer world from time to time that in this and in our sister societies, both within and without the precincts of Burlington House, there exist bands of ardent workers who are fighting in this great cause, often in face of adverse influences arising directly or indirectly from public indifference or other causes, some of which I propose dealing with in this address.

To all who are familiar with the influence of scientific progress on the evolution of civilisation, that is, to all students of the history of modern science, the general want of appreciation of research here cannot but be a matter of profound wonderment. It is not my intention to attempt an analysis of the causes of this public apathy on the present occasion. We must, I am afraid, deal with it as an accepted fact. Attention has from time to time been called to this national weakness by the Press and by publicists whose influence should carry conviction to the lay mind. We can, no doubt, remember weighty utterances by statesmen such as the Duke of Devonshire, the late Lord Salisbury, Lord Rosebery, Mr. Chamberlain, Mr. Balfour, and, above all, in recent times, Mr. Haldane, who loses no opportunity of driving home the lesson of the importance of science and of scientific method to the national welfare. Nor have our scientific workers themselves failed to sound the note of alarm with all the authority of expert knowledge. But, in spite of these individual efforts, it cannot be said that we have made much headway; public interest in scientific research may still be considered to be on a low level—certainly lower here than in many other leading nations, and most decidedly lower than is desirable in the best interests of our country. A temporary flicker of excitement is caused when some sensational discovery is announced, or when some result of immediate practical (commercial) value is made known, but even in these cases the interest taken is only transitory and is narrowed down to the immediate issue; the broad cause which makes such results possible is lost sight of. The steady, plodding work which culminates in great discoveries is being carried on quite unheeded by the general public, and the workers themselves are practically unknown outside the ranks of science. Research as a "cult" is not understood; the national attitude towards the workers is one of "payment by results" in the very narrowest sense of the term.

How this state of affairs is to be remedied is a knotty question which I confess appears to me somewhat hopeless of solution at the present time. It may be that by persistent attack from within and the pressure of competition from without the country will, in fact must sooner or later, awaken to the situation. It may be that science will have to become more self-assertive and make its influence felt as a political power. There is need here, as has been often suggested, for a Minister corresponding to the "Minister of Public Instruction," or the "Cultus-Minister" of other countries. The newly-formed "British Science Guild" may fairly be expected in the course of time to help us in raising the level of public opinion towards the importance of research, this being, in fact, one of the primary objects for which this organisation has been founded. It is safe to assert that any individual or organised body of workers, however zealous, who undertake this mission will have a Herculean task to perform. But, in the meantime, while waiting for the era of public enlightenment, there must be no pause in your search for new knowledge; there is no need to call a halt; there are boundless "regions yet untrod" awaiting your enterprise. The imperial view of research which I am advocating will add zest to your labours if you consider that by your individual efforts you are helping forward the general cause which we all have at heart. The new recruits which our little army of research chemists has gathered into its ranks are missionaries in this cause and active witnesses to the truth of the doctrine that the creativeness of its scientific men is one of the most precious assets which the country possesses. It is perhaps unnecessary to qualify this statement with the caution that I am not advocating a policy of bluster or of exaggerated self-assertiveness towards the non-scientific laity, or the equally objectionable policy of constituting ourselves a mutual admiration society. The temperament of our countrymen may, happily, be depended upon for keeping them clear of the danger of assuming an attitude which is both derogatory to science and damaging to its status in the public estimation. At the same time, it is impossible to survey the achievements of our little army of workers during the last decade without coming to the conclusion that neither in zeal or originality, nor in any of the qualifications which have enabled other nations to advance the cause of chemical science, are we lacking in this country.

THE JUBILEE OF THE FOUNDATION OF THE COAL-TAR COLOUR INDUSTRY AND ITS LESSONS.

The exaltation of scientific research into an abstract principle or "cult," which is the keynote of the remarks which I have put together for your consideration on this last opportunity when I shall have the honour of addressing you from the Presidential Chair, is, of course, a familiar subject to all who keep in view the objects of a society such as this. If I venture to formulate the principle somewhat more emphatically on this occasion, it is that the international gathering, which took place here last summer in honour of our distinguished past-President, Sir William Perkin, and in celebration of the jubilee of the foundation of the coal-tar colour industry, has given rise to many considerations which are intimately associated with the subject of this address. Although at that memorable assembly the voice of the nations was raised in gratitude for and in recognition of the numerous benefits arising from the establishment of a great industry, we must not forget that below the chorus of praise and congratulation, so justly sounded in honour of the founder, there was flowing an undercurrent of thought which, in some of the addresses and speeches, found verbal expression—the thought that this industry owed its existence to scientific research, and that it had been developed into its present magnitude by the never-ceasing applications of research. Certainly, Perkin himself has never lost an opportunity of driving home this lesson either to his scientific colleagues or to the general public. I have no desire to exalt the coal-tar industry into a position of undue prominence, although I have myself served an apprenticeship thereto, but it is now quite notorious that no branch of modern industry has ever furnished such a striking object-lesson in the application of scientific research to industrial progress.

I confess that there was sore temptation in sketching the outlines of this address to take advantage of last year's jubilee, in order to treat specifically of the history of the coal-tar industry from the point of view of the bearing of pure scientific discovery upon its progress and development. It is thought by many who are acquainted with this chapter in the history of chemistry that there is still scope for such a thesis. On the present occasion, however, it is perhaps better to avoid handling a topic which must necessarily be more or less technical, especially in view of the fact that this aspect of the subject has already been dealt with to some extent by chemists, many of whom are well qualified to speak with expert authority. It is only necessary to remind you of the addresses delivered before the German Chemical Society in 1890 in honour of Kekulé, on the occasion of the celebration of the foundation of the benzene theory; of the Griess obituary notices by Hofmann, Emil Fischer, and Caro, published by the same Society in 1891; of Caro's well-known lecture on the industry, delivered before the German Chemical Society in 1892; of the Hofmann memorial lectures, delivered before this Society in 1896 by Lord Playfair, Sir F. Abel, Dr. Perkin, and Dr. Armstrong; and of the recent lecture by A. v. Baeyer, given in honour of the Perkin jubilee. Speaking generally, it may be said that all the great steps, the new departures in the industry of coal-tar products, have been the outcome of pioneering work carried on in the first place without immediate reference to practical results. All honour to those who have developed these results into manufacturing operations, but honour in the first place to the scientific pioneers! This is the real lesson taught by the celebrations of last July. It may be of interest to consider in the next place how far this lesson has been learnt here on the one hand by the scientific public and on the other by the general public.

That the lesson has not been learnt by those who are most immediately concerned, the manufacturers themselves, is sufficiently apparent when we compare the enormous development of the industry in Germany with its comparatively small development here and its decadence in France, once an active centre and a successful competitor with us in the manufacture of coal-tar colouring-matters. This, I am fully aware, is a sore topic with our manufacturers; but, unfortunately, the facts are only too obvious. A recent paper by Dr. James T. Conroy on "The Chemical Trade of England and Germany—a Comparison" (*J. Soc. Chem. Ind.*, 1906, 25, 1011) will be found very instructive by those who require later statistical details. With respect to the public attitude, it may be said that such appreciation of Perkin's work as was expressed through our Press was just what might have been anticipated in a country where the true position of scientific research is imperfectly understood. The rejoicing was over the purely practical achievement—the discovery of the convertibility by chemical processes of so many otherwise useless tar products into saleable articles of commerce. The public cannot, as matters now exist in this country, go behind such proximate results. Moreover, the limitation of the appreciation in this way brings out very clearly the difficulties which must be encountered in any attempt to raise the status of scientific research in general, and of chemical research in particular, in the national estimation. Consider, by way of contrast, the works of the *littérateur* or artist; these appeal directly to the public or to some section of the public, and can be appreciated according to their merits. Not so the labours of the scientific investigator; his achievements are measured solely by the utilitarian standard; he is, as I said before, paid strictly by results. In other words, while Literature and Art have taken their position as "cults" in all civilised nations—a position to which they are fully entitled—Science is judged by a lower and narrower standard, and certainly cannot be said to occupy in this country the same position as its sister branches of culture.

With respect to our own branch of science, Chemistry, it may be especially said that it is not generally recognised that the so-called "practical" achievements are few and far between; that they do not spring already perfected from the fertile brain of some "inventor," but are always led up to by numerous discoveries which, according to the national standard of valuation, would be considered worthless. The jubilee celebration of last summer is particularly instructive from this point of view. I do not think that it was at all realised by the public that the rejoicing on that occasion was over something more than the discovery of mauve and the foundation of a new industry. Those representatives of our science who were present could have told the nation that the founder of that industry had half a century ago vindicated the claims of pure scientific research to take rank as a real power spelling prosperity in the hands of those who have learnt the lesson of how to use it. They could have told the public also that while the accidental discovery of mauve in the course of a scientific attempt to synthesise quinine was not in itself a very remarkable achievement, that chance observation happened to be made by a young man who was prompted to try the experiment by legitimate deduction, and who was so imbued with the spirit of research that he followed up the hint thus given with true scientific method and developed a laboratory preparation into a factory product involving the use of raw materials which had never before been made on the large scale, and which had been discovered by previous generations of chemists who could never have dreamt that their results would be raised to the importance of being of "practical" use. So, also, it could have been pointed out that while Perkin himself never manufactured more than some half a dozen colouring-matters during his connexion with the industry, the total number now on the market being about 1,000, he had synthesised scores of compounds, and had made other discoveries of no commercial value whatever but which are of no less importance, in fact, are really of greater scientific importance, than the half-dozen dyestuffs made at Greenford between 1856 and 1873, and which would lose none of their interest for us had mauve never been discovered and the coal-tar colour industry never called into existence. It may be said in brief that it was the principle of research that was being honoured in the person of one of the great pioneers in the application of chemical science to chemical industry, and that the gratitude expressed by the nations was not alone for the material benefits arising from the industry, but equally for the enormous impetus which the new branch of manufacture gave to the development of pure chemistry, this being a chapter in the history of our science now, of course, familiar to all students of that history, but which certainly remained unread by the outer world at the time of the gathering here last July.

Although giving special prominence to the scientific aspect of the work of our distinguished colleague, I am most anxious to avoid the imputation that I am depreciating the industrial side of his particular achievements or the application of chemical science to industry in general. My contention is for the principle that scientific research, like every other branch of human culture, is worthy of national homage, whether it leads to immediately "practical" results or not—that its position in the scale of civilising agencies is not dependent upon such occasional stimulants as the jubilee of the foundation of a new industry or the announcement of a sensational discovery which furnishes materials for newspaper paragraphs. It would, I think, be generally admitted that any country which limited its appreciation of research to such branches of science as were likely to lead to industrial developments was on a low level in the scale of civilisation. It happens—perhaps I may add fortunately for us—that our particular science has its utilitarian side, but that is, so to say, a happy accident which has in many ways promoted our cause. I may remind you that in our Charter a kind of utilitarian excuse had to be found for granting the privilege of incorporation to the original body of members, that excuse being that Chemical Science is "intimately connected with the prosperity of the manufactures of the United Kingdom, many of which mainly depend on the application of chemical principles and discoveries for their beneficial development," and that the Chemical Society had further for its object "a more extended and economical application of the industrial resources and sanitary condition of the community." But, as you all know, the enormous development of our subject has necessitated the formation of other societies dealing with the industrial and professional sides of chemistry, and although we have now limited our work to the primary object, "the general advancement of Chemical Science," the Fellows of this parent Society are none the less cognisant and appreciative of the activity and efficiency of those other organisations to which we have given rise in the course of our history.

In maintaining the principle that scientific research has been, is being, and can always be carried on independently of its practical applications, I have no desire to give countenance to the view, somewhat prevalent, I fear, in this country, that there is some kind of antagonism between pure and applied science; that the scientifically trained chemist, for example, and the "practical" man, instead of being allies, as they should be, are in opposition. The days when such notions were held are, happily, passing away; if but slowly in this country much more rapidly abroad. My plea simply amounts to a claim for the readjustment of the positions of pure and applied science in the public estimation. The course of industrial development in the future is bound to become more and more interwoven with the development of pure science, and the perpetuation of erroneous ideas on this point cannot but act injuriously on both causes. In our own domain it is absurd to suppose that there is any antagonism between the two aspects of chemistry. Far from this being the case, it may safely be asserted from the experience furnished by the coal-tar industry that the rate of progress is actually measurable by the degree of substitution of pure science for empiricism. Those manufacturers who fail to recognise this principle do so at their own peril; those who have realised its truth cannot but admit that the more enlightened views respecting the function of science in the factory have been largely due to the influence of Perkin's work and example half a century ago.

CHEMICAL RESEARCH IN EDUCATIONAL AND MANUFACTURING CENTRES.

Having thus attempted to give expression to the views of chemists concerning the position of research, I will, in the next place, venture to submit the question whether the output of work, to which attention was called in the early part of this address, is really representative of the productive capacity of the nation, and, if not, whether there are retarding or deterrent causes in operation tending to check the progress of chemical research in this country. In dealing with this part of the subject, a few preliminary considerations must be made clear. In the first place, although we comprise within our ranks practically all the active workers, we cannot lay claim to be the only publishers of original chemical research in Great Britain. Some distinguished authors, as we know, have contributed their papers to the Royal Society, the Royal Society of Edinburgh, the Royal Irish Academy, the Cambridge Philosophical Society, the Manchester Literary and Philosophical Society, and other publishing bodies, or have published directly through some scientific magazine or journal. Our workers occasionally also send their results to the German Chemical Society for publication in the *Berichte* or to the French Academy for publication in the *Comptes rendus*. I have taken the trouble to look into the question of the publication of chemical papers by British chemists through channels other than our Transactions and Proceedings, and have come to the conclusion that such an overwhelmingly large proportion of the work done is communicated to our Society that we may justly claim that our publications are fairly representative of the total activity of the country in the way of research. I will remind you further that such papers as do appear in our pages have, as it were, received the stamp of originality or fitness for insertion in our journal by being filtered through the Publication Committee, and I think we may legitimately claim also that the standard of quality thus insured has, on the whole, been maintained at a high level. In the next place I would urge that, as we have in the past fulfilled and are now carrying out that primary object for which the Society was founded, it is our solemn duty to look upon ourselves as the custodians of chemical research in this country, and that we are bound, at least morally, if not by virtue of any executive powers, to safeguard and look after the interests of research whenever and wherever it may be carried on, and to take cognisance of any deterrent causes that tend to hamper its progress. In giving publicity to the opinion that there are many such antagonistic influences in operation here, I am not in the smallest degree attempting to minimise the value of the work which is being done. On the contrary, when we consider what has been and is being accomplished in the face of serious obstacles, and often at the cost of great personal sacrifice, the value of the achievements becomes enormously enhanced and the sterling quality of our workers is brought more vividly into prominence. The question actually before us is whether we are getting as much in the way of original investigation as might fairly be expected in view of the potential research talent known to exist in our ranks. If, as I maintain, this is far from being the case, it may be at least useful, even if no definite remedial measure can be enforced, to examine into and make known publicly the causes leading to this suppression of talent. It is confessedly a very large subject to deal with adequately in the course of an address, and the task is by no means lightened by the reflection that however strong a case can be made out in support of the conclusions at which we may arrive, we have no power in our corporate capacity to insure compulsory action for the amelioration of the present state of affairs. We are not in the position of a church militant, declaring a crusade against scientific unbelievers, neither can we exert the influence of a trades union and proclaim a strike among our workers. All that we can do is to direct attention to the retarding influences in the hope that a public expression of chemical opinion may lead to some improvement in the existing conditions.

In dealing with the question under consideration, the first point to which attention must be directed is the character of the institutions in which research is being or might be expected to be carried on. We may begin with such establishments as those which have been built and endowed, and are being maintained for the specific purpose of enabling research to be conducted under favourable conditions, like the Royal Institution and the Davy-Faraday Laboratory, founded by Dr. Ludwig Mond. Then, also, there are certain public establishments like the Royal College of Science, the Central Technical College, maintained by the City and Guilds of London Institute, University College, London, the Government Laboratory, the Imperial Institute, the Pharmaceutical Society, and the Research Department at Woolwich, which, although not primarily founded for the prosecution of abstract research only, have helped to enrich our science by the publication of results obtained in their laboratories. To these may be added certain semi-private establishments, founded in connexion with particular industries, such as the Lawes Agricultural Station, to which the Goldsmiths' Company has recently made the munificent grant of £10,000, the Wellcome Research Laboratories, and the Guinness Research Laboratory. The Lister Institute also must be regarded as a contributing laboratory. To all these centres of research our science is indebted for many notable advances, and beyond expressing our gratitude to the founders, supporters, and workers in the various laboratories, I have nothing to do with these institutions excepting perhaps to point out that many of them are most inadequately endowed and supported, in view of the national importance of the work which they enable our active chemists to carry out.

After giving to these institutions and establishments all the credit to which they are justly entitled, there remain two other groups of centres in which research might be expected to flourish. I refer to educational establishments and to factories. With respect to the latter, it may be said that any research which is conducted in their laboratories is for trade purposes, and that they could not reasonably be expected to give publicity to the results. This is a perfectly fair contention as far as it goes, and the consideration of factories as centres of research might very well have been regarded as beyond the province of this Society. I should not have ventured to touch upon this point here were it not that it is in reality most intimately bound up with the other aspect of the subject under consideration, viz., the part played by educational establishments in furthering chemical research in this country. This connexion will, I hope, be made clear in the course of the subsequent remarks.

Turning to educational centres, we have in the first place the Universities, University Colleges, and Institutions of University rank. A few of these, such, for example, as the Victoria University at Manchester, where a recognised school of chemistry has been created, and Cambridge, whence contributions of importance reach us from time to time, are doing good service in the cause of chemical research, as witnessed by the pages of our publications. From other University laboratories, also, we receive occasional communications, these being for the most part the work of the professors. But with the exception of Manchester, it cannot be said that in any of our Universities has there been called into existence an active centre of chemical research—a "school" in the Continental sense of the term. I do not propose dealing in detail on this occasion with the very large question of the position of research in our Universities, but putting the case broadly, we should, I think, all agree that after making allowance for the few noteworthy exceptions, the actual contributions to our science from these centres are far below the standard, both of quality and quantity, which might be expected and which we should all like to see attained. If any doubt on this point should exist, it is only necessary to call to mind the productive activity in the Continental Universities as compared with our own. Judged by this standard, there can be only one conclusion—that many of our Universities are distinct failures as centres of chemical research, and that the total output of work from University laboratories is by no means worthy of the great traditions of this country as a pioneering nation in scientific discovery. The most discouraging aspect of this conclusion is that, in spite of the enormous development of our science during the three-and-twenty years that have elapsed since the presidency of Sir William Perkin, I find myself making practically the same complaint that he made from this chair in 1884 (Trans., **45**, 219). If these seats of the highest learning, called into existence for the dissemination and promotion of knowledge, can give such a comparatively poor account of their achievements in chemistry, it is evident that there must be deterrent causes at work. It would be going beyond my province to attempt a detailed analysis of these causes here; they are numerous and not easy to deal with in a limited time, but some of them are of the same nature as those affecting the position of chemical research in other educational centres which I propose discussing immediately. They may be summed up under such headings as ancient traditions, defective educational methods, want of sufficient means leading to the frittering away of the research faculty by the drudgery of "coaching," the poor outlook for chemical research as a career, and the pedantic notion that a subject requiring for its advancement something akin to manual labour is derogatory to high scholarship. Behind these causes is the general public ignorance of and apathy towards research, to which I referred at the outset, and if I may paraphrase the utterances of recent authorities in the educational world, over them all is the trail of the examining board.

In dealing with the next part of the subject, the newer educational institutions, I must crave indulgence while I invite attention to a few personal reminiscences, for it so happens that I am in the position of a connecting link between the old and the newer state of affairs in the educational world. Entering the Royal College of Chemistry, in Oxford Street, as a student in 1866, I found that Hofmann had just left this country, and I never had the advantage of coming under the direct influence of that great teacher. But the spirit of research which he had called into existence pervaded that institution, and we all know that under his inspiration a school of brilliant chemists was formed—a body of men who have left their mark upon English chemistry, both in its scientific and industrial aspects. Many of Hofmann's pupils are, happily, still with us, and it would be invidious to give a list of names; suffice it to say that many of them have occupied the chair from which I have the honour of addressing you.

At that time the prospects of a career for a scientifically trained student were not very promising. Apart from the various branches of engineering, there was no great demand for scientific men in the constructive or productive industries. Electricity had not then developed into a branch of applied science, and, although chemistry was the only science that had a direct bearing on manufactures, the number of openings in factories or in educational establishments was very limited, and the outlook for a young chemist who had to depend upon his knowledge of this subject for his living was not very hopeful. I well remember that when my own inclinations towards chemistry were under consideration, the pinnacle of success was supposed to be only attainable by becoming what was known as an "analytical chemist," a definition used to discriminate between the scientific chemist and the pharmacist, the latter, as I may remind you, having then, as now, the right to the designation "chemist." It is true that the foundation of the coal-tar colour industry by Perkin in 1856 had given a great impetus to chemical training as a means of achieving industrial success, and it is well known that large numbers of students were attracted to chemistry as a career by this discovery. But by 1866 the excitement caused by the introduction of mauve and magenta and their successors had subsided, and it certainly cannot be said that the throng of zealous students who filled the laboratories in Oxford Street were altogether drawn there by prospects connected with the discovery of new colouring-matters. The influence at work in filling these laboratories was, as we have been frequently told, Hofmann's personality—his zeal and genius as an investigator and his brilliancy as a teacher. It was his reputation as a great explorer into the regions of the unknown that attracted many, perhaps most of us, into that Institution the destinies of which he had guided, and the one great aim of those who were launched upon their career under this inspiring influence, or under the traditional influence that long survived his departure from this country, was to find some opening in life where opportunities would be given for following the lead of the great master by contributing something towards the advancement of their science. But, as I have said, the chances of finding suitable openings were few, and it did not fall to the lot of many of us to find such opportunities. Some by stress of circumstances had to utilise their training for breadwinning purposes as soon as possible after leaving the College; others, also imbued with the spirit of research, could find no career giving scope for the development of this faculty, and were perforce compelled to expend their energies in other directions.

The state of affairs which I have outlined above persisted for many years, and in fact the conditions have not very much changed for the better down to the present time. There were but few centres of research activity in the country, and the appointments connected with these were so badly paid that other branches of more lucrative work had also to be carried on in order to make research work possible. The factories had, more or less, failed as centres for the scientific activity of trained research chemists, and the private institutions or educational establishments offered opportunities for but a very small fraction of the would-be chemical investigators. It is not surprising that in such a chilly atmosphere the spirit of research did not flourish very vigorously. A few zealous workers kept the torch alight, often at great personal sacrifice, and it is of interest to note in passing that one set of institutions from which much original work formerly proceeded, namely, the laboratories attached to some of the hospitals, have gradually declined as research centres. In view of this state of affairs with respect to the general position of research and the limited outlet for the exercise of this faculty, it will be readily understood that the new departure in modern education, which is known as the technical education movement, was hailed with most sanguine expectations by all who had at heart the scientific prestige of this country. The first step taken towards the serious development of this phase of education is due to our City and Guilds of London Institute, under which endowment evening classes were started in the Cowper Street Schools in 1879, and later a day department, which became an established part of the scheme on the opening of the Finsbury

Technical College in 1883. The Central Technical College was opened in 1885. It is not for me to touch upon the work of our own Institute; the President of this Society is, *ex-officio*, a member of its Council and Executive Committee. I only refer to the foregoing dates because of the bearing of the work of the Institute on the later development of technical education. The Acts of Parliament of 1889 and 1890 placed, as you know, large sums of money at the disposal of counties and county boroughs for the purpose of furthering technical education, and there can, I think, be no doubt that the successful pioneering work of the City and Guilds of London Institute had to a very great extent prepared the way and created an atmosphere of public opinion favourable for the development of the new movement. Out of that movement there has sprung into existence a number of institutions classed here as belonging to the "Polytechnic" type, of which there are no less than twenty-three in and around London and about 110 in the provinces.

In stating that this new departure was at first regarded as a hopeful sign of the times, it is not difficult to put ourselves in the position of those chemists who were watching the course of events some twenty years ago. It was known that in ability our workers were not inferior to those of other countries; it was known that the research spirit was dormant here, but that owing to defective and obsolete methods of education and other causes this available source of national prestige and prosperity was being very largely squandered away. Here were new institutions coming into existence for the avowed purpose of improving the industries of this country; they were unfettered by ancient traditions, and ahead of them was the spirit of modern progress encouraging development along the right lines. Surely it was not unreasonable to expect, and it was confidently anticipated by most of us, that in these laboratories there would be formed new centres of research—that the outlook for the scientifically-trained chemist would be distinctly improved. I know, as a matter of fact, that at the outset of the new movement numbers of young men of high ability and full of zeal were attracted towards these institutions by the prospect of finding themselves in a favourable environment for extending the boundaries of their science. This movement had confessedly for its primary motive the improvement of the technical skill and knowledge of scientific principles of the artisan classes, but this most praiseworthy object did not appear to be, nor is it necessarily incompatible with, the prosecution of research. So far as we are concerned, I do not imagine that many dissentient voices will be raised when I state that if it was contemplated that the chemical industries would be improved in the same way that other industries would be advanced the movement began at the wrong end. In our particular subject it is, I think, generally recognised that the main hope of advancement is from above and not from below—that it is with the leaders and not with the rank and file that rests the prosperity of this country in the way of chemical manufactures.

If we now ask whether the modern educational development has fulfilled our expectations with respect to the advancement of chemical science, I for one must confess to a feeling of profound disappointment. There may be better times ahead when that era of public enlightenment dawns, but at present, with a few notable exceptions, these twenty-three London polytechnics are, on the whole, so little productive that we may discount them as active centres of research. It must be remembered, moreover, that this class of institution has spread all over the country, and that the total expenditure in the way of money and teaching energy is so great in comparison with the output of original work that chemists have every right to ask why this state of affairs should exist. I may remind you that only a few years ago, when the University of London was being organised, the late Sir Michael Foster published an article on the polytechnics, the main gist of which was to urge upon these institutions the necessity of developing research; if any justification for my own note of disappointment is necessary, it is to be found in the circumstance that such an appeal should have been necessary at all.

Turning now to the consideration of the causes of this failure on the part of the new educational establishments, I must, in the first place, guard myself against the imputation that I am disparaging their work. The most acute form of disappointment is that which is experienced when we find weakness where we had looked for strength, and in emphasising their weakness from our standpoint I am not shutting my eyes to their usefulness in other directions. It is not a depreciation of the work which they are doing if we deplore their failure in another branch of work which they might be doing. From what I know of these institutions, and from information furnished by very good authorities, I am satisfied that in some directions, and more especially in connexion with engineering and trade subjects and handicrafts—in all of which the artisan is an important element—they are doing a certain amount of good to the various industries concerned. But the danger for us is the general tendency in this country to ram the whole scheme of education into one mould, utterly regardless of the fact that the requirements of, let us say, an engineer are quite different from those of a chemist. It is for this among other reasons that our subject has suffered both in its scientific and industrial aspects, because the time and energy of the teachers of chemistry in these institutions are so largely frittered away in what might be called inconsequential labour on behalf of a class of student quite unprepared by previous training for assimilating the principles of our science and for the most part unable to give sufficient time to the subject to acquire any real working knowledge of it.

It must be remembered also that most of the work of these institutions is carried on in the form of evening classes; in some few of them day classes are also conducted, the day and night classes being taught by the same staff. It is no matter for wonderment that with such burdens imposed upon the teaching staffs the new departure in technical education has failed to create centres of chemical research. The failure is not due to the want of ability on the part of the teachers; there are, as we know, many men of proved competency on their staffs, and many more would be attracted were the conditions made more favourable. The defect is in the constitution of the governing bodies, which bodies largely reflect the popular attitude towards research and on which our subject is, for the most part, altogether unrepresented or else swamped by the predominating influence of those with whom the handicraft view of education is paramount.

There is another factor to be added to those which are acting detrimentally towards the cause of research in these institutions, and that is the want of sufficient endowment. I am afraid that it is characteristic of our countrymen to neglect the most important interests until they are forcibly awakened to their danger and then to try and make up for past neglect by rushing precipitately into the first plausible scheme that is presented. There is no doubt that the new educational development suffered much at the outset from this characteristic mode of procedure. The wrong kind of person was often allowed to frame the educational policy; the financial strength was exhausted in buildings and equipment, and the efficiency of the staff given only secondary consideration. We, of course, know that success in such educational work depends entirely upon the individual teacher—that the best mode of creating a school of chemistry, or any other subject, is to follow the advice of the late Sir William Flower with regard to the establishment of a museum: "First find a curator and let him build his museum around him." Had this principle been more generally adopted the new institutions might by this time have been playing a really important part in the development of chemical science and chemical industry. As matters are, inadequate provision for maintenance having been made, the general standard of educational work is lowered in order that the grant-earning requirements of some examining board may be met, and as a result the establishments have to be run as purely business concerns. This influence makes itself felt in many ways detrimental to our cause. In the first place, there is introduced that most baneful system of teaching the subjects in "classes" so that a syllabus qualifying for some particular examination may be gone through in a certain time. It is quite unnecessary to point out here that individual originality or the spirit of research can never exist in such an atmosphere. And the most serious aspect of the case is that, not only is a subject taught in this way never really assimilated so as to become a living principle with the student, but, what is far worse, the teacher himself, however original and zealous at the outset, is bound, after running in this groove, sooner or later to undergo deterioration. That is one of the reasons why the polytechnic movement has produced such a very small effect upon chemical industry, and has been to all intents and purposes a failure so far as concerns the advancement of our science.

There are other minor evils acting as retarding influences with respect to our subject and arising from the same cause, namely, the necessity of conducting these newer institutions, more or less, as commercial establishments. The prevalence of the "business" spirit among the committees and governing bodies gives an exaggerated importance to what may be called the office staff—the registrars and clerks. The work of the office staff is capable of being appreciated by the average committeeman, while the work of the scientific staff is generally beyond his comprehension, excepting so far as it can be measured by financial gain to the institution. The principals of these institutions are, it is true, always men of scentific training, and, by the way, generally engineers or physicists; with the one exception of the Sir John Cass Technical Institute there is no chemist at the head of any of the London polytechnics. But the principals, however enlightened may be their individual views, are still answerable ultimately to their governing bodies, and that is equivalent to the statement that they are more or less subservient to the business interests of the institutions. Now, I am not decrying the business faculty as such; it is an essential qualification for the proper government of any educational establishment, and I am afraid that many of our scientific workers and teachers are very much lacking in that faculty. But that is no reason why the teaching staff should be, as is frequently the case, subordinated to the office staff. It is not sufficiently realised that men of business and administrative ability are by no means rarities while really good teachers of science are much scarcer, and men who combine both the qualifications of a good teacher with the inspiring zeal of an original investigator are rarest of all. Now if, as was professedly the case, the modern departure in technical education had for its object the improvement of the industries, then it is sufficiently well known to us here that the future of our subject is with the men of the latter class, and the joint exertions of all the registrars and clerks, backed by the efforts of the most skilful chemical pedagogues who get through their syllabus within the session and earn the largest grants or score the highest percentage of successful "passes," will never raise the level of this country either in chemical science or chemical industry.

There is another practice which must be considered as injurious to our cause and which is familiar to all who have watched the progress of the technical education movement of late years, this also being the obvious result of insufficient endowment. I refer to that statistical standard by which the success of these institutions is chiefly if not absolutely judged. There is a tendency to measure the capabilities of the teachers by the number of students attending their courses, a criterion which, from our point of view, is both fallacious and mischievous. The fact that certain industries, and especially those connected with electrical engineering, have so largely fed the classes of the newer institutions cannot be interpreted as indicating that the teachers of these subjects are better qualified than the teachers of chemical subjects. The skilled artisans who derive benefit from theoretical instruction in subjects with which their everyday occupations make them practically familiar, are very much more numerous than the corresponding class engaged in chemical occupations. Perhaps it would be nearer the truth to say that in the latter there is no class of students exactly comparable with those representing engineering occupations in the polytechnics. At any rate, no comparison of relative merits of teachers, or of importance of subjects based on purely numerical statements, is of real value, and where such a standard is insisted upon the effect is obvious—the teacher is forced to compete with subjects which are really not comparable and so aims at numbers; he fills his classes with students whose numbers are accounted for not by zeal for becoming proficient as chemists, but by the promise which the subject offers as a means of scoring examinational success. Here again is there degradation of teacher and of subject, and the spirit of research is naturally stamped out under the treatment. As a matter of pure political economy, if it is desired to benefit the chemical industries of this country through the polytechnics, it would be better to make a selection from the chemical staffs of these institutions, to relieve these men from all teaching, and to subsidise them to the same extent for carrying on original work. I venture to think that both science and industry would gain by the change.

It is sometimes stated that it was never contemplated that research should be carried on in these institutions—that this was the duty of the higher educational establishments. So it is the duty of the higher educational establishments, but the very fact that these are enabled to discharge their duty in a most imperfect way should have stimulated the newer institutions to make every effort to redeem our credit by making adequate provision for research. I will not venture to intrude my opinions concerning the vitalising influence of research upon other scientific subjects, but with regard to our own I have not the least hesitation in declaring the belief that a school of chemistry which is not also a centre of research is bound to degenerate and to become a mere cramming establishment not worth the cost of the maintenance. It is easy enough to follow the actual course of the degeneration process in such an institution. The teacher, who may be a man of real ability and who has entered with the hope of finding time and opportunities for research, finds himself, sooner or later, in the position of a chemical schoolmaster. The predominance of the business influence in the institution not only leads, as I have already indicated, to the lowering of the level of the instruction and to his own consequent degeneration, but he is, as a further consequence, so overweighted with business and administrative work that these, superadded to his teaching duties, leave him neither time nor energy for original work. The spirit of research within him is strangled by officialism and his teaching faculties deadened by the monotonous toil of the annually recurring drudgery of routine teaching. He has not even time to educate himself by keeping in touch with the progress of his subject, and one of two things must happen; if he remains at his work his research faculty is lost to the country and his teaching becomes less and less efficient as he falls more and more behind the actual state of knowledge—he undergoes submergence. Or, as the other alternative, he abandons the career at the first opportunity and is replaced by another teacher who undergoes the same process of submergence, or, what is more generally the case, the good teacher is replaced by an inferior one because the reputation of the institution as a centre of research is not such as to attract the highest class of teacher.

The scale of remuneration also does not enable these institutions to command the services of the best teachers, although I do not think that this is the chief deterrent cause, as there are numbers of young chemists of first-rate training and ability who would be quite willing to devote their time at the outset of their career to acquiring teaching experience in these establishments, even at some personal sacrifice, if facilities for research were given. In the present state of affairs one can only marvel at the fact that so many men of ability can be found willing to take service in these newer institutions, the more especially as, apart from the absurdly inadequate remuneration often given to the chiefs of the chemical departments, the payment of the subordinate members of the staff is generally on a scale which is nothing short of a scandal to the wealthiest of European nations. Considering the long course of training necessary to produce a competent teacher or demonstrator, and in view of the actual amount of work expected from these men who, by virtue of their attainments and position, are compelled to live up to a standard of high respectability, it seems almost incredible that the average scale of remuneration should not exceed the wages earned by an artisan and is often below that standard. It is instructive from this point of view to note the advertisements which appear when these posts have to be filled and to compare the qualifications required, the duties expected, and the salaries offered. This state of things is, unfortunately, not confined to the newer institutions, and an inquiry into the salaries paid to assistants and demonstrators throughout the country will show that in many of the older educational establishments there is the same inadequacy of payment. The practical result from our point of view is again the crippling of the research faculty; the chiefs are inadequately supported, and the subordinates have to work overtime as examiners, or in some other capacity, in order to make a "living wage." It is needless to say that under such conditions there is wholesale destruction of research talent going on to the ultimate detriment of our country.

I have thought it desirable to deal at some length with the shortcomings of the newer institutions, because the older educational centres have been so frequently castigated without effect, that there should be some hope of bringing about an improvement in the position of chemical research in establishments which, in principle at least, profess to meet the latest educational requirements in applied science. It will be remembered that at the outset of the movement the late Prof. Huxley encouraged the foundation of these newer institutions by describing them as "capacity-catching" appliances—machines for sifting out the national talent and passing it on to higher work. I do not for a moment imagine that our great leader ever contemplated that capacity would be caught by these appliances in order to strangle it. Yet that is virtually what is going on to a very large extent under the enforced conditions of teaching our subject to which I have called attention. According to the "Official List of Appointments" published by the Institute of Chemistry last year there are on the staffs of the London and suburban Polytechnics about fifty-four trained chemists. To these may be added 237 engaged in teaching in similar institutions in provincial centres throughout the United Kingdom. In one respect the hopes of those who expected great opportunities for chemists from the new departure in technical education have been realised. At the present time there are in this country in round numbers some 290 posts available for teachers of chemistry, which posts have actually been created by the latest movement in technical education. If now we ask whether the output of original work from these 130 centres is representative of the productive power of the 290 teachers, there can, I think, be only one answer, and that an emphatic negative. An examination of the lists of teachers in these centres shows that only about twelve out of the total number are carrying on research, and most of these in a desultory way. It is evident that there is justification for my complaint that there is this submergence of creative faculty going on all over the country; the nets have been spread and the capacity has been caught, but so far with comparatively little effect upon the development of new schools of chemical research.

The next question, whether the influence of the newer institutions upon chemical industry has realised our expectations, is intimately connected with the educational side of the subject with which I have been dealing. No institution which runs classes in chemistry for examinational purposes only and which affords no opportunities for research to its teachers can be expected to produce any serious effect upon the industry, and it is not surprising that the manufacturers should look with suspicion upon such products of modern technical education. It is extremely difficult to obtain information as to the kind of chemical student attending these newer institutions in various parts of the country. The majority —I should say by far the larger majority—are preparing for a certificate or a degree, and not for the purpose of becoming working chemists. Speaking from my own experience, I can say with regard to evening students in institutions which are not fettered by any examinational requirements, that a certain amount of good has been done in isolated cases. I could name foremen and managers in chemical works whose promotion has been the result of their attendance at evening classes, and I could name teachers who have become converted from pure pedagogues into really efficient teachers by attending the practical laboratory courses. But institutions of this type are, it must be remembered, in a very small minority, so small that they may be left out of consideration in dealing broadly with the relationship between modern technical education and chemical industry. The question really before us is whether the small amount of good effected by the newer institutions as a whole is not achieved at too great a cost in the way of individual originality—whether it is worth sapping the vitality of two or three hundred teachers of chemistry so as to leave those of them who possess the research faculty without time or energy for such work in order that a few foremen here and there may be improved in position. So far as chemical science is concerned we can only deplore this squandering of our most precious asset; so far as concerns chemical industry I venture to think the result is too trifling to be worthy of serious consideration.

It is not easy to get accurate information as to the actual numbers of chemists employed in factories in this country. In the first place, many of our manufacturers dignify with the name of "chemist" any human testing machine in their employment, and there is no doubt that many men whose daily occupation does not go beyond the valuation of a few staple products or raw materials are described as chemists. In 1902 a Committee of the British Association published a statistical report on this subject, in which are set forth the numbers of "chemists" engaged in the different branches of chemical industry and the kind of training which they had received (*Brit. Assoc. Report*, Belfast, 1902, p. 97). According to the returns furnished to this Committee the total number of chemists in those factories which supplied information is about 500, and Sir James Dewar, in his Presidential Address for that year (*loc. cit.*, p. 15), on the authority of Prof. Henderson, gives as a liberal estimate a total of about 1,500. Whatever the actual number may be, it appears from the report that evening classes, together with analysts' and works' laboratories, supplied only a total of eighty-five, so I think there is justification for the contention that the effect of the newer institutions upon chemical industry is quite insignificant.

The consideration of the question of the position of factories as centres of research is, as I have previously stated, intimately bound up with the educational side of the subject because we have to deal now with the educational establishments which are supplying the chemists for our factories. We must really include also among these the foreign Universities and Technical Schools, because many of the works' chemists employed here were educated abroad. It is not my intention now, nor is it essential to the point under consideration, to institute a comparison between the merits of the English and foreign-trained chemist. We are, I am sure, all agreed that the only men likely to be of real use in chemical industry are those who, starting from a sound, general education, have been through a systematic and organised course extending over at least three years and followed, if possible, by some experience in research. For those who are to become leaders in the industry the research training is, I should say, absolutely indispensable. Thus it is only institutions in which this kind of work is going on that need be taken into consideration, and it is because so few of the newer institutions here are doing this kind of work that they have, as I have already pointed out, more or less failed in that object for which they were specifically founded. Now our Universities do not profess to cater especially for the training of industrial chemists, although a few of their graduates have found careers in factories. The later development of departments of applied science at some of our Universities, such as Leeds and Birmingham, is certainly a move in the right direction and one from which great good to particular industries may be expected to follow. It would be impossible for me in the time at my disposal to attempt to deal with the large and important question of the kind of training which the chemical student should undergo, or with the question of the suitability of this, that, or the other curriculum. The bare fact that about forty out of the total number of chemists employed in this country were, according to the report already quoted, educated in foreign Universities or Technical Schools, shows that there must be some superiority in the foreign system. The numbers of English, and I may add American, students in the foreign Universities bear testimony to the same effect.

The feeders of the chemical factories are thus the Universities and Technical Schools, British and foreign, and the question before us as the custodians of research is whether the absorption of the chemical talent from these sources by the factories is justified from the industrial point of view—whether these products of modern training, having entered into such careers, are being used to the best advantage. In other words is that wastage of original faculty which, as I have endeavoured to show, is going on in the educational institutions going on also in the factories? Now, I have already pointed out that any original work done in a factory for trade purposes is no concern of ours, and it will be readily understood that great difficulty would be encountered in any attempt to get accurate information on this point. But in view of the circumstance that so many teachers of our subject are devoting their lives to this very work, that we are ever on the alert for that most precious research faculty in order to train it and to add it to our national assets, we are, I believe, justified in asking what becomes of these men when they enter the ranks of industrial chemists? Whether the total number of chemists employed in our factories is what it should be is a point for the manufacturers themselves to consider. Even the extreme estimate of 1,500 does not seem a very large chemical staff for the whole of the factories of Great Britain. In the German colour industry alone, according to information supplied to us seven years ago as Jurors for the Paris International Exhibition, five of the great factories were employing 557 chemists—real scientific chemists and not mere testing machines such as are dignified with the name of chemist in many of our factories.

From my own experience as head of the chemical department of a Technical College, and with some knowledge of the requirements of chemical industry, I can state that the newer technical education when conducted in the form of organised courses of day instruction extending over several years has enabled us, according to Huxley's metaphor, to capture a large amount of chemical capacity. I have no doubt that others attached to similar institutions can supplement and extend my own experience. During twenty-two years' connexion with the Finsbury Technical College I estimate that in round numbers from 300 to 400 trained students have been made over to the chemical world. Add to those the students from other institutions doing similar work and it will be seen that the supply of chemical talent available for science and for industry is very large. In giving these figures it must be remembered that they refer to *bona-fide* chemical students, young men who have gone through the course with the definite object of making chemistry either a profession or a trade. Now of the total output of trained chemists from the various institutions a fair proportion—a number quite equal to the average in other countries—are possessed of the research faculty. We have seen what becomes of this when such men throw in their lot with the educational establishments. Are not we, the teachers, justified in asking whether the prospects of developing this faculty in our factories are such as might be reasonably expected from the known requirements of chemical industry?

In answer to this question I am afraid we must come to the conclusion that here also there is an enormous submergence of research talent going on. It is true that the position is improving—that some of our more enlightened manufacturers have realised the value of such men, and by taking advantage of their faculties have improved their various industries. But these cases are as yet exceptional, and the ideal will never be reached until the research laboratory becomes a recognised and well-staffed department in every chemical factory. Do our factories possess departments which can honestly be described as centres of research in the sense, say, of the research laboratories of the German colour factories? I am afraid not; indeed, I know of scores of young men of great promise and ability who have been swallowed up by the factories and gradually degraded, in the chemical sense, into mere machines carrying out routine work which really required no elaborate chemical education for its effective performance. There is, of course, no satisfactory means of measuring the influence of the newer education upon the chemical industries of this country, and we can only speak from individual experience concerning the careers of our own students. It is upon this experience that I base the conclusion that our country is wasting its resources in a most reckless way so far as concerns the chemical industries. There is an enormous amount of talent available if our manufacturers would only utilise it in the right way. It has frequently been pointed out how, on the Continent and in America, the educational establishments and the industries are brought into relationship by the co-operation between the manufacturers and the teachers. Only last week in his lecture at the Royal Institution Prof. Lunge again drew attention to this point in forcible terms. Here, so far as chemical industry is concerned, such co-operation is practically unknown, and, as a consequence, there exists more or less distrust where there should be confidence, and both the educational and the industrial sides of our subject are crippled. This is perhaps the most powerful influence at work in this country in checking that development which follows normally from co-operation between the representatives of science and of industry.

We cannot profess, nor is it possible for any educational establishment, British or foreign, to undertake to supply men with an expert knowledge of any particular branch of manufacture. We can only say when asked for such, "We can supply you with men of general knowledge of principles and possessed of originality and resourcefulness; take them into your factories, put them into research laboratories where they have a free hand, make them acquainted with the problems awaiting solution in your industry, and do not be too impatient for immediate results; in the long run such men will justify their appointments." That this ideal utilisation of the national chemical faculty is not going on to the extent that it ought appears to me to be shown in two ways. I may be possibly opening the door for controversy here, and so it is better to state at once that I am not raising the vexed question of the imperfections of our Patent Laws. But I do not think it can be reasonably questioned that in the present state of chemical literature the patent list is, on the whole, a very fair measure of the research activity in the factories, and from that point of view it is quite unnecessary to do more than invite a comparison between the discoveries in the way of chemical products and processes emanating respectively from the British and foreign factories. The other criterion of research activity is furnished by the Society of Chemical Industry—an excellent organisation of which we are all justly proud. That Society does for applied chemistry what we are doing for chemical science; it provides an arena for the announcement and discussion of new discoveries in industrial chemistry, and it gives publicity to the results in the pages of its Journal. Now it is no disparagement to the work of that Society to say that the contributions to its Journal representing the total results of research conducted in the factories of this country are exceedingly meagre. That, of course, is no fault of the Society as a Society, but the paucity of original communications may be taken in conjunction with the revelations of the patent lists as a justification of the complaint that in the factories, as in the educational establishments, there is going on this same wastage of the research faculty.

CHECKS TO THE WASTAGE OF THE RESEARCH FACULTY; RESEARCH FUNDS AND SCHOLARSHIPS.

Turning now from the consideration of the various deterrent influences, we may in the next place deal with such counteracting agencies as are available in this country. It is clear, from our point of view, that any means by which the research faculty, having once been captured, can be given free scope for development must be a distinct gain to our cause. All who have had to do with the training of chemical students must in the course of their experience have come across young men of exceptional talent as original workers. Fortunately for the intellectual vigour of the nation this faculty is not a class distinction, and is to be met with occasionally in all ranks. Possibly the lower ranks have the advantage, but the actual facts can only be arrived at by Galtonian methods. We are concerned more particularly with the utilisation of this faculty for the promotion of our science and with the maintenance of the principle that the submergence of this faculty means so much dead loss to the national resources. Now it unfortunately happens that many of the men thus gifted come from stations in life which render it imperative that they should proceed at once from the college to some bread-winning occupation. A few may perhaps be lucky enough to find appointments in which there is scope for the development of their faculties, but I am afraid the majority do not; they undergo that process of extinction as original workers which I have already dealt with. I could point to large numbers of cases illustrative of this most deplorable waste of productive energy, and other teachers could, no doubt, do the same. One of the most valuable counteracting agencies, and one the importance of which, from our standpoint, cannot be overestimated, is that system of awarding research scholarships to men of proved ability so as to enable them to carry on original work after finishing their college training. The value of this most rational method of endowing research is due mainly to the fact that the right men are captured in the right way; they are not, as it were, squirted promiscuously out of an examination mould, but they are selected by the teachers who have had them under observation during the whole course of their training and who know their real as distinguished from their examinational capabilities.

This method of promoting science and at the same time giving the crowning touch to the scientific education of the best products of our educational establishments is of such national importance that we should fail in our duty did we not place upon record our high appreciation of those agencies which are working in this direction. Unfortunately they are few. The amount of capital required for the adequate endowment of such scholarships is necessarily large, and the public spirit of our countrymen very rarely expends itself in this direction. But I desire especially to name among others the scholarships given by the Royal Commissioners of the 1851 Exhibition, the Salters' Company's Research Scholarships, the Schunck Research Fellowships, and the Carnegie Research Scholarships, all of which are doing excellent service in the cause of chemical research in this country, as may be seen from the pages of our publications. Of the value of these endowments there can be no question, and with respect to the Science Scholarships of the 1851 Exhibition I can speak from personal experience, having for many years been one of the examiners of the reports presented by the scholars. These last scholarships are not limited to chemical subjects, but our science claims, on the whole, the largest number of scholarship holders. But, although we should probably be unanimous in our estimate of the importance of such endowments as these, there is another aspect of the case to which, I think, it right to call attention, if only for the opportunity it affords for answering certain objections to the specialisation of work rendered necessary by devotion to research.

It has sometimes been urged by educational authorities whose opinions are entitled to serious consideration, that it is unfair to students at the close of their general education to place temptation in their way by furnishing means whereby they are induced to devote perhaps some years to specialised research of no bread-winning value in their ultimate career. It is not difficult to answer this objection, although there may conceivably be conscientious teachers who on this ground would discourage post-graduate research work. In the first place, if the educational value of research be admitted, as it assuredly will be, it must necessarily be limited to some special field, and if, as is so generally the case, the student on the completion of his curriculum has no definite views as to his future line of work, it is obviously impossible to specialise his researches with reference to his prospective career. We can only proceed on the general principle that research in itself is of the highest disciplinary value in whatever career the student may ultimately adopt as a chemist—whether he becomes a teacher or a technologist; it being, of course, understood that no specialisation is permitted until the general scientific education has been completed on a broad and sound basis.

The question is whether this principle is a sound one, and as a matter of experience I have no hesitation in answering that question in the affirmative. The faculties called forth by research work, although for the time being concentrated on one particular problem, are just those which are essential for success in any branch of our subject. The nature of the particular line of investigation by which those faculties have been trained is in reality a subordinate point, subject entirely to personal conditions; that is to the special nature of the work with which the professor or teacher is associated. In cases where a choice of centre is possible the research student would naturally go to that institution where the work was in a field in which he was most interested or towards which he was attracted as affording a good preparation for his future career. But even where no choice of centre is possible, and where an opportunity for continuing research work in his own college after passing through the general curriculum is furnished by agencies such as those to which I have referred, the value of the student is enormously enhanced by the experience. The man and the subject are both gainers, and from my own knowledge of the careers of students who have availed themselves of such scholarships I have no hesitation in expressing the view that it is the duty of all teachers who are afforded the opportunity to encourage in every way the utilisation of these endowments. It is the teachers who are the real capacity catchers; it is their duty out of loyalty to our science and in the best interest of those who are taking to chemistry as a career to see that these available sources of productiveness are made the most of, and I again emphasise the indebtedness of the country to the founders of these scholarships.

The other agency working against the stream of adverse influences is to be found in the various funds from which grants are made to individual workers for the prosecution of particular researches. There are three such funds available for the promotion of chemical research, the Government Grant Fund of the Royal Society, the grants distributed annually by the British Association, and the income derived from our own Research Fund. Of these the two former have to be distributed over every branch of science, and chemistry takes its chance with other subjects. The total amount available for chemical research is not very large, and all who have served on the committees of any of these funds know very well that the amount applied for is generally much in excess of the sum available for distribution. The main difficulty of administration is, in fact, the equitable pruning of the various applications.

With regard to the results obtained through the Research Fund of this Society, the present occasion is in every way opportune for calling attention to our achievements and to our needs. The history of this fund is fully given in our Jubilee volume, published in 1891, and it is, therefore, unnecessary to recapitulate that history now. The income derived from this fund has hitherto enabled us to distribute annually a sum of about £220—a very modest amount considering the number of claims and the activity of our workers. Of the value of the assistance thus given we are, of course, all thoroughly aware here, but it may not be generally realised by the outer public what an enormous amount of good work is being promoted by tho judicious administration of this very modest income. In order to get at the actual facts, Mr. Carr has been so good as to prepare a table covering the eight years from 1898 to 1905 inclusive, and setting forth for each year the sum granted, the number of grantees, the total number of papers published by the grantees in our Journal or elsewhere, and other particulars which will be found in the table itself.* From this it appears that 151 grantees during that period published 203 papers, thirteen failed to publish, ten have not yet published, and eighteen grants are still in the hands of the grantees. The total amount granted was £1,770, so that for this expenditure we have actually given to our science 203 papers, and more may be expected from those who still have grants in hand or who have not yet published their results. The figures as they stand, and even if nothing further is achieved, show that the grants average from £8 to £9 per paper, and, as we all know, each paper represents the results of at least one and frequently of several years' work. Moreover, in many cases the sums allotted are of more than subsidiary assistance; some of our workers are practically dependent upon these grants for procuring the necessary and often costly materials required for their researches, and without such support would be unable to carry on their work. It is not going too far to say that there are no funds giving such substantial returns for so small an expenditure as these Research Funds, and their importance as aids to the advancement of knowledge cannot be overestimated.

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* See Appendix B, p. 659.

I have thought it desirable to set forth the results accomplished by our Research Fund on this occasion, because several points and considerations connected with this branch of our work have arisen during the past year. It will be remembered that one of the objects which the promoters of the Coal-Tar Colour Jubilee celebration embodied in their scheme was the establishment of a Research Fund to be administered by this Society in association with the name of the founder of the industry, Sir William Perkin. As the causes acting detrimentally to the progress of research in this country have been so fully considered in this address, I cannot refrain from calling attention to a very remarkable attack upon that part of the scheme which appeared in one of the technical journals.* That a discordant note should have been sounded by a countryman of Perkin's at a time when foreign nations were co-operating loyally with us for the realisation of the objects set forth by the promoters will appear almost incredible to posterity when the proceedings of that great international gathering have passed into the domain of history. The answer to that attack was, of course, given in the theatre of the Royal Institution last July in terms which form a very striking comment upon the views expressed by the writer of the letter in question, and as a further practical refutation I am glad to be able to announce that a net sum of about £2,700 will be added to our capacity-catching resources in the form of a "Perkin Research Fund," that sum having been raised by international subscription in honour of our distinguished past-President. It was also, as you are aware, my pleasing duty last month to announce a further contribution of £1,000 from the Goldsmiths' Company for the promotion, through our Society, of research in Inorganic and Metallurgical Chemistry.

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* *Journal of Gas Lighting, etc.*, June 5th, 1906, p. 648.

I will venture in conclusion to dwell upon another aspect of the work of our Research Fund which must, I am afraid, in the present state of affairs be regarded as purely hypothetical. At some future period the hypothesis might possibly become practically verified—it is entirely a question of means, and, unfortunately, of very large means; but I am most anxious to bequeath to my successors in this chair at least the tradition of the desirability of realising the views which I have long held on this subject, and so I take advantage of this last opportunity of addressing the Society in the capacity of President to formulate these views with some emphasis.

Let us consider, in the first place, the actual resources at our disposal for the promotion of research. With the additional capital by which our fund has been increased the total income available for grants will be about £330 per annum. In view of the demands upon that income it is obvious that even now we are possessed of but very limited means, and that the Research Fund Committee will still be compelled, as has hitherto been the practice, to allot the grants for the purchase of materials or special apparatus. This mode of allotment has been recognised as a principle by the Committee for many years, and in view of our slender resources no other course is possible. Administered on this principle the fund has been, as I have already stated, of enormous value in the past, and it is to me a matter of the greatest satisfaction in retiring from the Presidency to know that during my period of office the substantial increase of our resources will enable us to extend the sphere of usefulness of the fund in the future. But, in addition to the promotion of research by the means indicated, there is another, and, according to my view, an equally valuable method for assisting our workers in the prosecution of their researches, and that is the allotment of personal grants to enable the grantees to secure skilled assistance—to purchase, in fact, the services of human material as well as chemicals and apparatus. It is only want of sufficient income that has hitherto debarred the use of our fund in this way; the Government Grants administered by the Royal Society are, as you are aware, allotted to applicants in certain cases for such personal assistance, and the great desideratum of our Research Fund is a sufficient augmentation of capital to enable us to do the same kind of work.

I am so confident that an extension of our means towards this end would be productive of a most notable increase, both in the quantity and quality of the chemical research done in this country that I have no hesitation in placing upon record the opinion that the next step taken in the forward policy of the Chemical Society ought to be in this direction. To do much good in the way of making personal grants we should, of course, require to capitalise a very large sum; we want an income of thousands instead of hundreds, and I confess that I see no immediate prospect of realising this dream. But there can be no doubt that for those who have the interests of our science at heart there could be no better method of subsidising research. In strengthening the hands of workers by such means the efficiency of the capacity-catching machinery would be increased in the best possible way, both for the subject and for the individual. The active worker is the best of all possible selecting agents; the assistant chosen by him could be depended upon as being a man of proved competency, and possibly of his own training. The assistant so selected would benefit largely by his association with the active worker; he would rise in the scale of competency with increasing experience and might in his turn be expected to become an active centre of research. Supposing grants of this order were made possible to our Society, there would be added to the influences already referred to another power tending to check that dissipation of the research faculty which, as I have endeavoured to show, is going on to such a deplorable extent throughout the country.

The general conclusion which appears to be justified by this inquiry into the position and prospects of chemical research is, that the position here is by no means as satisfactory as we could wish—that much more might be done if the conditions were made more favourable for our active workers. In view of the actual achievements, accomplished in spite of the existing disabilities, it appears that the prospects for this country as a home of chemical research have been improving during the last decade with greater rapidity than at any previous period in the history of our Society. But it is also obvious that there is much work yet ahead of us before the environment in which our workers find themselves is properly cleared from obstructions. The remarks which I have offered on this occasion may possibly be of use in indicating the directions in which such impediments are to be found.

APPENDIX A.—THE PUBLICATIONS OF THE CHEMICAL SOCIETY, 1895—1906.

	TRANSACTIONS.			ABSTRACTS I.		ABSTRACTS II.		PROCEEDINGS.		
Year.	No. of papers.	No. of authors.	No. of pages.	No. of Abstracts.	No. of Pages.	No. of Abstracts.	No. of Pages.	No. of Abstracts.	No. of Authors.	No. of Pages.
1895	116	109	1082	1190	692	1292	544	157	132	241
1896	117	108	1465	1201	716	1638	684	174	141	251
1897	114	109	1139	1049	648	1526	612	129	123	250
1898	102	100	996	1187	720	1639	660	151	121	252
1899	120	110	1166	1477	968	2140	828	172	148	244
1900	127	117	1160	1355	712	2403	780	180	152	231
1901	146	139	1340	1530	784	2224	712	180	161	266
1902	160	145	1575	1632	852	2222	712	194	165	255
1903	142	126	1460	1650	872	2232	768	151	157	292
1904	175	168	1714	1968	1072	2649	848	215	175	252
1905	184	168	1818	1727	956	2629	872	233	221	312
1906	186	183	1890	1745	1000	2796	912	236	215	326

APPENDIX B.—THE WORK OF THE RESEARCH FUND, 1898—1905.

Year.	Amount of Grants.	No. of Grantees.	No. of Papers in Trans.	No. of Papers in Proc. only.	No. of Papers published elsewhere than in Trans. Chem. Soc.		No. of Grantees who have not published papers.	No. of Grantees whose papers have not yet appeared.	No. of Grants not closed.	No. of Grants returned.
	£									
1898	245	22	24	2			3			
1899	192	13	23				2			2
1900	170	11	14				1			
1901	250	21	24	1			1			
1902	230	17	35	1			2		6	1
1903	232	19	17	3	2	Phil. Trans.; Proc. R. S.	1	1	2	4
1904	215	21	21	1	1	Ceramic Society.	1	2	5	1
1905	236	27	30	3	1	"Berichte."	2	7	5	2
Total.	1770	151	188	11	4		13	10	18	10

OBITUARY NOTICES.

FREDERIC JUST CLAUDET.

Born March 24th, 1826; Died April 19th, 1906.

Frederic Just Claudet was born at Choisy-le-roi, France, on the 24th March, 1826. He was the son of François Antoine Claudet, F.R.S., distinguished for his discoveries of the action of light on various substances in the early days of photography.

He was educated at University College, and subsequently entered the École des Mines, Paris, where he graduated with honours.

For some years he acted as assistant to Professor Graham, of the Royal Mint, in several important investigations, and in 1851 published the results of a special research on the cobalt amines. At this period the firm of Rothschild and Sons were engaged in establishing their Royal Mint Refinery for the treatment of gold and silver bullion, and Claudet was appointed to aid them in the work. Immediately afterwards he commenced practice in London as an assayer, analytical chemist, metallurgist, and mining engineer, and received the appointments of Assayer to the Bank of England and also to the Bank of France.

The arduous nature of this professional work left him but little time for research for some years, and when he again became an investigator it was in the field of chemical technology. The problem to which he specially directed his attention was the extraction of the small quantities of silver present in the cupriferous pyrites from Spain and Portugal, which were largely used in the manufacture of sulphuric acid, and in 1870 he had so far successfully overcome the difficulties attending its solution that he took out a patent for a process which bears his name, and by which the extraction of the silver from the liquors, obtained after roasting the burnt pyrites with common salt, by precipitation by a soluble iodide, could be economically effected. During this investigation a prismatic form of arsenic trioxide, existing as a distinct mineral in the pyrites, was discovered by him, and was named Claudetite by Dana.

As a chemist and analyst he was one of the most painstaking of men; almost, if that be possible, over punctilious in observing the most minute precautions in order to ensure accurate results.

He was elected a Fellow in 1852. For many years he had resided during the winter at Cannes, where he died on the 19th April, 1906.

William Gowland.

HERMANN JOHANN PHILIPP SPRENGEL.

Born Aug. 29th, 1834; Died Jan. 14th, 1906.

Dr. **Hermann Johann Philipp Sprengel**, F.R.S., who was found dead in his armchair on Sunday evening, January 14th, 1906, at his house in London, had long been a familiar figure in English chemical circles. Born on the 29th of August, 1834, at Schillerslage, near Hanover, the second son of George Sprengel, a landed proprietor, he was educated at Hanover, and after studying chiefly chemistry and physics at Göttingen and Heidelberg he took his degree at the latter university in 1858. He came to England in 1859, and for some time acted as assistant to Sir Benjamin Brodie at Oxford until, in 1862, he settled in London, where he was engaged in research work at the laboratory of the Royal College of Chemistry, and at Guy's and St. Bartholomew's Hospitals until 1864. From 1865 to 1870 Sprengel acted as chemist at the sulphuric and nitric acid works of Messrs. Thomas Farmer, then at Kennington, after which date he engaged in work chiefly connected with his own inventions and patents. Possessed of remarkable originality, he was the author of numerous inventions of scientific and practical importance, from none of which, however, did he derive any substantial benefit; in not a few instances he was in advance of his time, but it cannot be denied that he lacked the sense of proportion so essential to the successful man. The research by which he will always be known to posterity is that "On the vacuum" published in the *Transactions* in 1865. In this he describes the pump now universally known as the "Sprengel pump," the vacuum being produced by the fall of mercury, water, or other liquids in tubes. The mercurial pump exhausted vessels so that the residual air amounted to only 1/937920000 part of its original volume (*Chem. News*, 1870, **29**, 125), a degree of exhaustion far beyond anything previously achieved and never surpassed until Sir James Dewar recently introduced the use of charcoal cooled by liquid air as an absorbent of the residual gases. The Sprengel pump made possible the Swan and the Edison glow lamp (see the *Times*, January 2nd, 1880, and December 29th, 1879) and was made brilliant use of by Sir William Crookes in his work on the radiometer and by Professor Röntgen in producing his apparatus for demonstrating the rays called after his name. Graham, who employed it in his investigation of occluded gases, says of the Sprengel pump, "Indeed without the use of his (Sprengel's) invention some parts of the inquiry would have been practically impossible" (*Phil. Trans.*, **156**, 408), and every chemist knows to what excellent use Bunsen put this invention for accelerating filtration. Sprengel was an expert glass blower and his deft fingers stood him in good stead in all his work. Characteristic of the man was the simplicity of the means by which he achieved results of remarkable accuracy. Next to his pump in importance as a scientific intrument is to be reckoned the simple "U-tube" which he devised for the determination of the density of liquids, and which, as he points out in his paper, is applicable also to the exact determination of the apparent coefficient of expansion of liquids. Moreover, such is the delicacy of the instrument that the presence of as little as half a grain of dissolved mineral matter (such as carbonate of lime) in one gallon of water, or 7·5 milligrams per litre, can be ascertained quantitatively (Trans., 1873, **26**, 577). Sprengel's researches on explosives were of the greatest public importance, and the world is indebted to him for his safety explosives, for his method of exploding semi-sensitive or hydrated explosives by cumulative detonation (now employed to detonate wet guncotton), and for his suggestion of the use of picric acid by itself as a powerful explosive, which, as melinite or lyddite, has greatly increased the influence of artillery in modern warfare. From none of these inventions did Sprengel derive any pecuniary benefit, and it is therefore not surprising that, especially in his latter days, he should have been very sensitive when his discoveries were attributed to others, who reaped where he sowed. Sprengel patented his safety explosives on April 6th and October 5th, 1871, but want of encouragement caused him to allow these patents to lapse. A fuller description of this work is recorded in the Transactions for August, 1873, and Sir Frederick Abel, in his presidential address to the Society of Chemical Industry in 1883, characterised it as "One of the most interesting, original, and suggestive of comparatively recent contributions to the literature of explosives." It would lead us too far to give full details of this paper. The broad principle of these explosives is the admixture of an oxidising with a combustible agent at the time of, or just before, their use, the constituents of the mixture being themselves non-explosive (*Proceedings of the Royal Artillery Inst.*, No. 4, Vol. XIV). Led by the idea that (as a rule) an explosion is a sudden combustion, Sprengel made these mixtures in such proportions that their mutual oxidation and deoxidation should be theoretically complete, and submitted them to the violent shock of a detonating cap (Trans., 1873, **26**, 799). A long list of combustible agents is given, of which may be mentioned solid or liquid hydrocarbons such as naphthalene, phenol, benzene, &c., but Sprengel prefers the use of nitro-compounds which produce cold when mixed with nitric acid, thereby avoiding the heat generated when hydrocarbons are used. As oxidising agents he enumerates hydrogen peroxide, nitric anhydride, nitric peroxide, potassium chlorate, &c., and even pure or elementary oxygen in either a solid or a liquid form is referred to. He prefers, however, the use of nitric acid, because it is cheap and a common article of commerce. The mixtures are to be exploded by fulminate detonators wrapped in dry guncotton, and to this method Sprengel gave the name of "cumulative detonation." He especially points out that picric acid alone contains a sufficient amount of available oxygen to render it, without the help of foreign oxidising agents, a powerful explosive when fired by a detonator, and that its explosion is almost unaccompanied by smoke. Sprengel had already exploded a mixture of picric acid with nitric acid containing 15 per cent. of water in March, 1871, at the powder works of Messrs. John Hall & Sons at Faversham. It is true that a *caveat* covering some of his explosive mixtures had been deposited on January 9th, 1871, at the American patent office by Silas R. Divine, but as its contents were only disclosed in 1885 (*Chem. News*, 52, 271, 295), this secret document can in no way jeopardise Sprengel's claim and merit of being the first inventor.

Another meritorious invention of Sprengel is contained in his patent of 1873, which refers to the introduction of water in a finely-divided spray in lieu of steam in sulphuric acid chambers. The introduction at that time of the Glover tower gave rise to the fear that too much heat would be abstracted to make the use of water feasible, and the water spray is only now coming into more general use.

The above are the more important of Sprengel's many contributions to science and practice. Active to the last, he had only recently lodged an application for a patent relating to the production of diamonds at high temperatures.

His eminence as a scientific worker was recognised by his election in 1878 to the Fellowship of the Royal Society, and this distinction, as well as the title of Professor bestowed on him by the German Emperor, was a solace to him in his many disappointments.

RUDOLPH MESSEL.

GEORGE BOWDLER BUCKTON.

BORN MAY 24TH, 1818; DIED SEPT. 25TH, 1905.

ELDEST son of the late George Buckton, of Oakfield, Hornsey, Middlesex, who was Proctor of the Prerogative Court of Canterbury, Doctors' Commons, the subject of this memoir was privately educated, being debarred from entering a public school by an accident in boyhood which crippled him for life.

Upon the death of his father he removed to London (Queen's Gardens, Hyde Park), and in the year 1848 entered the Royal College of Chemistry, Oxford Street, where he remained nearly seven years, and for the latter part of the time acted as Research Assistant to the Professor, Dr. A. W. Hofmann, with whom eventually he published two joint papers, entitled "Researches on the Action of Sulphuric Acid upon the Amides and Nitriles, together with Remarks upon the conjugate Sulpho-acids" (*Proc. Roy. Soc.*, 1854, and Trans., 1856).

Previous to this, however, he was engaged in studying the platinum bases, which formed the subject of three papers read before this Society, namely:

1852. "Deportment of Diplatosammine with Cyanogen."
1853. "Double Chlorides containing Diplatosammonium."
1855. "The Platino-tersulphocyanides and the Platino-bisulphocyanides."

Later contributions, also in his own name, and equally, if not more, important, were:

1857. "On the Isolation of the Radical Mercuric-methyl" (*Proc. Roy. Soc.*).

1858. "Some of the Products of Oxidation of Chinese Wax" (Trans.).

1859. "Isolation of the Organo-metals: Mercuric, Stannic, and Plumbic Ethyls" (*Phil. Trans.*).

1861. "On Stib-ethyls and Stib-methyls" (Trans.).

About this period Buckton, being already a member of the General Committee of the British Association, attended the meeting in Aberdeen, 1859, where he read a paper "On Pentethyl-stibene"; and also that held at Cambridge, 1862, for which he prepared a communication entitled "The Formation of Organo-metallic Radicals by Substitution."

In 1865 Buckton published the last of his chemical papers, this time in conjunction with Professor Wm. Odling, "Note on some Aluminium Compounds" (*Proc. Roy. Soc.*). It was in this year that he married Dr. Odling's sister and removed to Haslemere, Surrey, where he had purchased the estate of Weycombe, and built for himself a house after his own design with an adjacent astronomical observatory. Here on the slopes of Hindhead he resumed his study of entomology, for which he had shown a decided taste in boyhood, and published several important works and monographs on that subject.

Buckton was elected a Fellow of this Society in 1852, serving for two periods in the Council, 1855–6 and 1865–6. He was elected Fellow of the Royal Society in 1857, and subsequently became a member of the Linnean and Entomological Societies. He continued to a certain extent his chemical studies in the Surrey home, as he had a good laboratory, and gave several courses of elementary lectures to the young people of the neighbourhood. He was interested in astronomy, photography, electricity, and other branches of science; making for himself a Wimshurst machine, and sundry telescopes, grinding and mounting his own reflectors. He also contributed to *Nature* a a few practical notes—1885, 1887, 1892.

It is a matter of wonder and admiration that Buckton accomplished so much under great physical disadvantages; accentuated, moreover, by another unfortunate accident which happened in the year 1882, when he broke his leg in attempting to close the roof shutter of his astronomical observatory. He found time to give his attention to local affairs, being for many years a manager of the National Schools, of numerous flower-shows, &c., only resigning active participation within a few years of his death. He was also a good musician and an excellent artist, painting both in oils and water-colour; these tastes he kept up until the very end of his life, being engaged in water-colour sketching after his eighty-seventh birthday. His genial character and engaging manners inspired all who had the good fortune to become acquainted with him. The family motto, "Veritas," was well exemplified in his case throughout a long and well-spent life.

His cremated remains were interred in Haslemere Churchyard on September 30th, 1905, in the presence of the members of his family and a very large gathering of personal friends. He leaves a widow, one son, and five daughters. J. Spiller.

LXI.—*The Hydrolysis of Amygdalin by Acids.*

By Robert J. Caldwell, B.Sc. (Lond.), Leathersellers' Company's Research Fellow, and Stephen Lewis Courtauld, B.A. (Cantab.).

The discovery that amygdalin may be resolved into a molecule of glucose and one of mandelonitrile glucoside, made by E. Fischer in 1895 (*Ber.*, 28, 1508), served to confirm the view put forward by Hugo Schiff in 1870 (*Annalen*, 154, 337) that amygdalin is derived from benzylidenecyanohydrol and a biose. Judging from the fact that the hydrolysis is effected by an extract of dried brewer's yeast (of the Frohberg type), Fischer came to the guarded conclusion that amygdalin is a derivative either of maltose or of a quite similarly constituted diglucose. The tendency has been to overlook Fischer's *caveat*, in spite of the fact that amygdalin is rapidly and completely hydrolysed by emulsin, which is without action on maltose; indeed, Dunstan and Henry, in summarising the present state of knowledge of such glucosides, in their recent British Association Report (*York*, 1906) on the chemical aspect of cyanogenesis in plants, speak of amygdalin as "probably the maltose ether of benzaldehydecyanohydrin."

We have undertaken the study of amygdalin at Professor Armstrong's request, especially on account of its abnormal behaviour towards enzymes. The action of acids is described in this communication.

It was first pointed out by Ludwig, in 1856 (*Jahresber.*, 679), that the action of a hot dilute solution of hydrogen chloride is similar to that of emulsin, both giving rise to benzaldehyde, hydrogen cyanide, and glucose, some formic acid being also produced when acid is used. No measurements of the rate at which the hydrolysis is effected by acid have been published as yet.

The method we have adopted is that which was used by one of us, in conjunction with Dr. E. F. Armstrong, in measuring the rate at which lactose undergoes hydrolysis (*Proc. Roy. Soc.*, 1904, 73, 526). Using a normal solution of hydrogen chloride it was found that the hydrolysis took place, at a measurable rate, only at 60° and above. The use of stronger acid was undesirable, as it is well known that the hot concentrated acid gives rise to mandelic acid and ammonia. Our experiments were made at 60° and 80°.

Not only were polarimetric readings taken but the amount of benzaldehyde and of hydrogen cyanide produced was also estimated from time to time. In the case of the benzaldehyde, apart from analytical errors, only the earlier values are trustworthy, as on prolonged heating with the normal acid tarry products are formed.* The hydrogen cyanide values are necessarily low (especially at the higher temperature), some of the hydrogen cyanide being converted into formic acid, as noted by Ludwig. It should be stated also that the rotatory power is not an exact measure of the percentage of amygdalin hydrolysed, as no allowance can be made for intermediate products. An attempt was made to estimate glucose by titrating neutralised samples with Pavy's solution; it was found, however, that (probably as a consequence of the amygdalin being hydrolysed by the boiling alkali) a green coloration was developed which obscured the end point.

Hydrolysis of Amygdalin by a Solution of Hydrogen Chloride.—In all cases, the solution used contained 10 grams of amygdalin and 3·65 grams of hydrogen chloride per 100 c.c.; this solution had no odour of benzaldehyde after being kept during a week at room temperature; at 38°, the rotatory power changed from $-7°0'$ to $-6°28'$ in the course of a week, some benzaldehyde being liberated. A flask containing 250 c.c. of the liquid was completely immersed in a thermostat kept at $60° \pm 0·1$; at intervals, samples of 20 c.c. were withdrawn, cooled, filtered and then examined polarimetrically at 25°.

In estimating benzaldehyde, the method used was substantially the same as that described by Ripper (*Zeitsch. anal. Chem.*, 1902, **41**, 61), which consists in distilling the aldehyde by means of steam into a known amount of a standardised solution of sodium bisulphite and estimating the excess of bisulphite with standard iodine solution, using starch as indicator. It was found that this method gives results which are in agreement to within 1 per cent. provided the distillate be delivered under the surface of the bisulphite, the latter being kept cool by ice or circulating water. In making the experiments, carefully measured quantities of the acid solution, enclosed by sealing in thin test-tubes, were heated in the thermostat. From time to time these were removed; when cold they were broken up in a distilling flask, together with some water and sufficient calcium carbonate to neutralise the acid. The whole was then distilled with the aid of steam. At the end of half an hour the circulating water was shut off from the condenser and steam was passed through the tube for a few moments to remove any adhering benzaldehyde. Blank experiments in which steam was passed through a boiling solution of amygdalin during an hour proved that no benzaldehyde is liberated by this operation.†

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* There was no appreciable loss of aldehyde in blank experiments in which benzaldehyde was heated with normal acid during twenty-four hours.

† When these estimations were originally made, we did not sufficiently recognise that although this method gives satisfactory results with benzaldehyde alone, the values obtained are too high if hydrogen cyanide is also present.

To estimate hydrogen cyanide, the cooled samples were washed into a flask and neutralised with standard caustic soda, using methyl-orange as indicator; the hydrogen cyanide was then determined by titration with an $N/100$ solution of silver nitrate in slightly alkaline solution, following Liebig's directions.

Law of Hydrolysis of Amygdalin.—As the hydrolysis occurs at two points in the molecule which are considerably removed from each other, it was to be expected that the less stable junction of most of the molecules would be first broken, giving an intermediate product which would undergo hydrolysis at a slower rate. Hence it was not to be expected that amygdalin would obey the simple unimolecular law unless the second stage in the hydrolysis were incomparably slower than the first. As a matter of fact, if the change is calculated from the rotatory power, assuming it to be a simple mass action (unimolecular), the value deduced exhibits a gradual but steady diminution, thus showing that the non-hydrolysed material becomes increasingly stable; if, however, the last one-third only of the change is considered, the unimolecular constant, K_2, is a satisfactory expression of the rate of change, because at this stage practically all the amygdalin is hydrolysed and only the intermediate substance is undergoing transformation.

It will be seen on reference to the tables that the estimated percentage of benzaldehyde as well as that of hydrogen cyanide is less in the early stages of the hydrolysis than the percentage change in the rotatory power: whence it follows that the biose junction in amygdalin is more susceptible of attack than the mandelonitrile glucoside junction; in other words, the intermediate products are mainly, if not wholly, glucose and mandelonitrile glucoside. The constant, K_2, obtained for the last third of the change, therefore, expresses the rate at

TABLE I.

Hydrolysis of amygdalin at 60°.

Time in hours.	Hydrogen cyanide per cent.	Benzaldehyde per cent.	a_D.	Percentage change in rotatory power.	K_1.	K_2.
0	—	0·0	−7°0′	0·0	—	—
24	—	15·3	4 3	20·5	0·00414	—
48	—	29·1	1 40	37·0	0·00418	—
72	—	39·4	+0 19	50·8	0·00427	—
96	—	47·5	1 45	60·7	0·00422	—
120	44·2	46·5	2 49	68·1	0·00413	—
144	46·4	51·3	3 36	73·5	0·00401	0·00338
168	51·2	—	4 14	77·9	0·00391	0·00333
192	54·8	—	4 48	81·7	0·00386	0·00340
217	—	—	5 16	85·2	0·00381	0·00341
∞	—	—	+7 25 (calc.)		Mean	0·00338

TABLE II.

Hydrolysis of amygdalin at 80°.

Time in hours.	Hydrogen cyanide per cent.	Benz-aldehyde per cent.	a_D.	Percentage change in rotatory power.	K_1.	K_2.
0	0·0	0·0	−7°0′	0·0	—	—
2	14·2	—	3 5	27·2	0·0688	—
4	26·1	40·9	0 0	48·6	0·0722	—
6	36·3	53·5	+2 13	63·9	0·0738	—
8	46·0	60·7	3 37	73·6	0·0724	0·0681
10	52·6	68·3	4 39	80·8	0·0717	0·0684
12	58·8	—	5 20	85·6	0·0702	0·0662
14	62·4	(69·0)	5 53	89·4	0·0695	0·0663
16	65·5	(70·8)	6 17	92·1	0·0654	0·0662
∞	(48·2)	(60·2)	+7 25 (calc.)		—	—
					Mean	0·0670

which Fischer's glucoside underwent hydrolysis under the conditions of our experiments. Proof that this argument is a valid one would be given if it were possible to isolate Fischer's mandelonitrile glucoside by stopping the hydrolysis when half-way through; we have, in fact, succeeded in so doing.

Two experiments only are recorded in Tables I and II, these being selected as the most complete series of observations at each temperature. It will be observed that in calculating the values of K_1 and K_2 the theoretical final rotatory power is used, although this could never be attained in practice, as the prolonged action of the normal acid on glucose at 60° gives rise to secondary changes which are attended with diminution in rotatory power.

Influence of Temperature.—The mean values of K_2, representing the velocity at which the hydrolysis of Fischer's glucoside takes place at 60° and 80°, are 0·00338 and 0·067 respectively.

Assuming van't Hoff's exponential equation,

$$\rho t_2 = \rho t_1 \epsilon^{\frac{q}{2} \cdot \frac{T_2 - T_1}{T_1 T_2}},$$

to hold good for mandelonitrile glucoside, the value of "q" (the heat of formation of the "active part," according to Arrhenius, *Zeitsch. physikal. Chem.*, 1889, **4**, 226) is 35,200 calories, as compared with the value 34,200 calories for maltose with the same strength of acid.

Comparison of Amygdalin with Maltose.—Although the temperature coefficients in the case of the hydrolysis of amygdalin, as well as of Fischer's glucoside and of maltose, are so very closely allied, yet the actual velocities in the case of amygdalin and of maltose differ very widely. Experiments made by Armstrong and Caldwell in 1904 gave the value 0·000449 for maltose at 60·1°, using a normal solution of hydrogen chloride. This value, being expressed in "minute" units, must be multiplied by 60 to make it comparable with the figures in Tables I and II. The constant for maltose is thus seen to be 0·0269 at 60·1°. Now the initial value of K_1 in Table I, representing the velocity at which the hydrolysis of the amygdalin-biose takes place, is 0·00414; that is, the biose radicle in amygdalin is at least six times as stable towards acids as is maltose. This difference is so large that it cannot well be attributed to an inhibiting influence exerted by the mandelonitrile group: it must be taken as very strong presumptive evidence that amygdalin is not a maltoside but a derivative of one of the seven theoretically possible isomerides of that disaccharide.

Action of Emulsin on Amygdalin.—It was found as a mean of many experiments that an extract of 0·1 gram of Merck's emulsin made up in 100 c.c. of a 10 per cent. solution of amygdalin produced hydrolysis to the extent of 60 per cent. in eighteen hours, as measured by the benzaldehyde produced. We estimate that normal acid at the same temperature would act at about 1/700th of this rate, so that, weight for weight, Merck's emulsin is at least 25,000 times as active as hydrogen chloride. It is difficult to reconcile this result with the statement made by Tammann (*Zeitsch. physikal. Chem.*, 1889, **3**, 25) that amygdalin is incompletely hydrolysed by emulsin. Tammann's conclusion, however, was based only upon estimations of the amount of hydrogen cyanide which was liberated.

Experiments made with active emulsin extracts show that hydrolysis may be readily effected to the extent of 95·6 per cent., 96·8 per cent., &c., in the course of twenty-four hours. In one case, 0·2 gram of emulsin in 100 c.c. of a 10 per cent. solution of amygdalin produced hydrolysis to the extent of 98·2 per cent. in ninety hours, as measured by the change in rotatory power; in another experiment, in which half as much emulsin was used, after sixty-seven hours, 98·5 per cent. of the total benzaldehyde was liberated but only 86·1 per cent. of the calculated amount of hydrogen cyanide could be detected; in fact, estimations of the amount of cyanide liberated always gave a lower figure than estimations of rotatory power or of benzaldehyde. Hence Tammann's conclusion that amygdalin is not completely hydrolysed by emulsin, based upon his measurements of the amount of hydrogen cyanide produced, must be regarded as erroneous.

Incidentally, it may be noted that as the method adopted hitherto in determining the amount of a cyanogenetic glucoside in a plant is based upon the amount of hydrogen cyanide which is liberated, the estimate of the amount of glucoside present usually arrived at must be low.

Preparation of Fischer's Glucoside by means of Acid.—Fifty grams of amygdalin were dissolved and made up with 250 c.c. of a $2N$-solution of hydrogen chloride to 500 c.c. This solution was heated in a thermostat at 60° during seventy-two hours and then cooled. The acid was for the most part removed by means of lead carbonate (110 grams) and finally with silver carbonate. The colourless solution was evaporated down to a thin syrup under reduced pressure at 60° and extracted five times with twice its volume of boiling ethyl acetate. On concentrating the ethyl acetate solution, the bitter glucoside (about 8 grams) slowly crystallised in rosettes. When recrystallised twice from dry ethyl acetate, the product melted at 147—150°. A mixture of mandelonitrile glucoside, prepared according to Fischer's directions by means of yeast extract, melting at 144°, with the more nearly pure glucoside prepared by the acid method, melted at 144°. The specific rotatory power of our product was $-26.5°$ at 20°, the value given by Fischer being $-26.9°$; benzaldehyde and hydrogen cyanide were at once liberated on digesting our glucoside with emulsin.

Several large crystals were obtained with ill-defined ends which permitted of measurements being made round one zone. The principal faces were at right angles, showing the substance to be probably orthorhombic, a conclusion confirmed by the appearance in polarised light.

Chemical Department,
City and Guilds of London Institute,
Central Technical College, South Kensington.

LXII.—*Mandelonitrile Glucosides. Prulaurasin.*

By Robert J. Caldwell, B.Sc. (Lond.), Leathersellers' Company's Research Fellow, and Stephen Lewis Courtauld, B.A. (Cantab.).

Having obtained Fischer's mandelonitrile glucoside from amygdalin in the manner described in the preceding paper it appeared to be desirable to ascertain whether it should be regarded as the glucoside corresponding to amygdalin or as a mixture of stereoisomerides corresponding to the *iso*amygdalin into which amygdalin is converted by alkali (Dakin, Trans., 1904, **85**, 1512) and which is also formed from it by the action of strong hydrochloric acid. It was found that the addition of a mere trace of baryta conditioned an immediate and rapid alteration of the rotatory power, the lævorotation becoming almost doubled without change of sign. There was no evidence of hydrolysis; but the glucoside could no longer be isolated in the crystalline condition, either by concentrating the solution or by extracting with ethyl acetate.

In his original description of mandelonitrile glucoside, Emil Fischer (*Ber.*, 1895, **28**, 1508) states that he proposed to "attempt to isolate it from the obviously impure preparation which has been described under the name of 'amorphous amygdalin' or 'laurocerasin.'" Now laurocerasin has been obtained recently in the crystalline condition by Hérissey (*Compt. rend.*, 1905, **141**, 959; *J. Pharm. Chim.*, 1906, [vi], **24**, 537), and renamed by him *Prulaurasin*; it has a higher rotatory power than Fischer's glucoside. Moreover, a third isomeric form of mandelonitrile glucoside (*Sambunigrin*) has been separated by Bourquelot and Danjou (*Compt. rend.*, 1905, **141**, 598) from the leaves of the common elder (*Sambucus niger*); this substance has the same melting point as Fischer's glucoside but higher rotatory power even than Hérissey's prulaurasin from laurel leaves.*

Amygdalin has been isolated from bitter almonds, peach kernels, cherry-laurel kernels, plum stones, and the fruit kernel of the bird cherry; it is noteworthy, however, that all attempts to obtain it from the leaves of these plants and from many other leaves which yield hydrogen cyanide on distillation with water have ended in the production of an uncrystallisable syrup only slightly soluble in ethyl acetate but giving with emulsin the same products as amygdalin. To this substance the name "amorphous amygalin" was applied by Winckler. Lehmann, who analysed such a substance, gave to it the formula $C_{80}H_{67}O_{60}N$ and proposed to call it "laurocerasin," supposing it to be a definite compound of amygdalin and amygdalinic acid. From results which he has recently obtained with material prepared carefully from the bark of *Prunus padus* and from cherry-laurel leaves, Jouck has deduced the formulæ $C_{42}H_{60}O_{21}N$ or $C_{42}H_{62}O_{21}N$. The work of Schoonbrodt, who in 1868 obtained a small proportion of bitter acicular crystals from amorphous amygdalin by the use of alcoholic ether, appears to have been generally overlooked; this substance was doubtless the same as that recently isolated by Hérissey with so much skill from the same source, namely, laurel leaves.

In the case of elder leaves, the glucoside is not accompanied by the enzyme necessary to effect its decomposition, so that the presence of hydrogen cyanide in this plant had been overlooked; as a matter of fact, the cyanogenetic glucoside "sambunigrin" was obtained without difficulty, when once its presence had been demonstrated, by Bourquelot and Danjou.

The properties of the three isomeric glucosides are set out in the following table:

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* The production of hydrogen cyanide from a plant was long held to be an indication of the presence of amygdalin.

	$[\alpha]_D$.	M. p.	
Mandelonitrile glucoside (Fischer)	−26·9	147—150°	Crystallises readily from hot ethyl acetate.
Prulaurasin	−52·7	120—122	Hygroscopic, obtained crystalline with difficulty.
Sambunigrin	−76·3	151—152	Crystallises readily from hot ethyl acetate.

Dunstan and Henry speak of them in their Report (York, 1906) to the British Association in the following terms:

"If it may be assumed that they are different—and the evidence on this point is not as conclusive as is desirable, having regard to the difficulty of isolating these glucosides in a pure state from plants—the differences between them probably lie in the nature of the sugar residue and it is desirable that the sugars produced from them on hydrolysis should be carefully examined." They have since (*Bull. Imp. Inst.*, 1906, 4, 340) suggested that "possibly two or perhaps all of them may prove to be identical."

There can be no doubt that they are definite isomeric substances. As they are readily attacked by emulsin, giving benzaldehyde, hydrogen cyanide and glucose, it is evident that they are all compounds of the β-glucoside type and that the isomerism is not of the order which obtains between the α- and β-methylglucosides.

Prulaurasin, in fact, is entirely analogous to *iso*amygdalin; it is a mixture of the two stereoisomeric *d*- and *l*-mandelonitrile β-glucosides. Sambunigrin must be the β-glucoside of dextromandelic acid. The "mixed" derivative has a lower melting point; moreover, its rotatory power, as Hérissey has pointed out, is the mean of the rotatory powers of the other two glucosides. In the case of the biose derivatives, the dextromandelic acid modification is at present unknown, but a comparison of the properties of amygdalin with those of *iso*amygdalin shows that strict parallelism exists between the latter and prulaurasin:

	$[\alpha]_D$.	M. p.	
Amygdalin (trihydrate)	−35·51	200°	May be crystallised from an aqueous solution.
*iso*Amygdalin (dihydrate)	−47·6	125—140°	Hygroscopic, will not crystallise from water.

Preparation of Prulaurasin.—When lævomandelonitrile glucoside is dissolved in water and the solution is rendered very slightly alkaline with baryta or ammonia, the rotatory power falls rapidly from $[\alpha]_D$ −26·0° to $[\alpha]_D$ −53·7°; the latter is approximately the rotatory power of prulaurasin given by Hérissey. The conversion takes place with the utmost readiness at 25°, following the unimolecular law:

Time in minutes.	a_D.	$\frac{10^5}{t}\log_{10}\frac{a}{a-x}$.
0	$-3°53'$	—
9	4 11	(576)
35	4 35	660
65	4 53	678
80	4 57	631
110	5 8	688
∞	5 22	—

Five grams of Fischer's glucoside were dissolved in $N/500$ baryta; after six hours, when the rotatory power was constant at $[\alpha]_D - 53\cdot7°$, the solution was saturated with carbon dioxide and filtered. The liquid was then evaporated at 60° under reduced pressure and the residue was dried in a good vacuum at 101°. The powdered material dissolved with difficulty in boiling anhydrous ethyl acetate, from which it was precipitated as a syrup by dry ether. This syrup crystallised slowly during the cold weather. The white solid thus obtained was more readily soluble in dry ethyl acetate than the original substance; it was again precipitated by dry ether and allowed to crystallise. The recrystallised glucoside was washed with the mixture of solvents, then with dry ether and dried in a vacuum over sulphuric acid. When prepared in this way, prulaurasin softens at 120° and melts at 123—125°. We are greatly indebted to M. Hérissey for having placed at our disposal a small quantity of the glucoside obtained from *Prunus laurocerasus*, which has enabled us to satisfy ourselves that this material is indistinguishable from the product made in the manner described from amygdalin. On mixing M. Hérissey's sample—which softened at 115° and melted at 118—120°—with ours, a mixture was obtained which melted at 116—120°. In grinding together the two specimens for melting point determinations, it was found necessary to exclude moisture by covering the material with dry ether, which was afterwards evaporated off in a vacuum. We have also prepared prulaurasin from Fischer's glucoside by the use of ammonia instead of baryta.

It is evident that Hérissey's product was not quite free from water, the value he gives for the rotatory power being slightly lower than ours, as is also the melting point. The analyses given by Hérissey also point to the presence of a little water in the glucoside.

The glucosides derived from racemic mandelonitrile are also further distinguished from the lævomandelonitrile derivatives by the properties of their acetyl derivatives, which are readily obtained with the aid of acetic anhydride. Amygdalin and *iso*amygdalin give hepta-acetyl derivatives; lævomandelonitrile glucoside and prulaurasin give tetra-acetyl derivatives. The acetylated mixed product in each case has the greater solubility in alcohol and the lower melting point:

	M. p.	$[\alpha]_D^{25}$. (5 *per cent.* *solution in* *ethyl acetate*).	*Character.*
Hepta-acetylamygdalin......	167°	−34·8°	Orthorhombic needles sparingly soluble in cold alcohol.
Hepta-acetyl*iso*amygdalin .	148	−35·5	Orthorhombic, soft needles somewhat soluble in cold alcohol.
Tetra-acetyl- Fischer's glucoside	136	−21·7	Orthorhombic, very fine, long needles, moderately soluble in cold alcohol.
Tetra-acetylprulaurasin ...	120—123°		Orthorhombic needles, extremely soluble in cold alcohol.

Hepta-acetylamygdalin.—This compound was prepared by Schiff (*Annalen*, 1870, **154**, 337), who omitted to state its melting point or its rotatory power. It is possible to effect complete acetylation of amygdalin by means of boiling acetic anhydride without the mandelonitrile radicle undergoing change; the product obtained from *iso*amygdalin by the same process is quite a distinct substance. Ordinary hydrated amygdalin is completely acetylated by boiling it during two hours with ten times its weight of acetic anhydride. The oil which is precipitated on pouring the cooled liquid into water solidifies quickly and when dried is readily purified by crystallisation from hot ethyl alcohol (95 per cent.). It crystallises in rosettes of colourless needles, which show extinctions parallel to the long edges and hence are probably orthorhombic. It is readily soluble in ethyl acetate or chloroform but very sparingly so in cold alcohol. It is not acted on by emulsin:

0·2073 gave 0·4089 CO_2 and 0·1021 H_2O. C = 54·12; H = 5·47.
0·2082 ,, 0·4151 CO_2 ,, 0·1028 H_2O. C = 54·35; H = 5·49.
$C_{34}H_{41}O_{18}N$ requires C = 54·33; H = 5·46 per cent.

*Hepta-acetyl*iso*amygdalin* crystallises in small, soft rosettes melting at 148°, which show parallel extinctions and are therefore orthorhombic. It is readily soluble in chloroform or ethyl acetate, and sparingly so in cold alcohol. This substance has a specific rotatory power which is very near to that of hepta-acetylamygdalin itself, but it is more soluble in alcohol; a mixture of the two substances melted at 141—144°:

0·2086 gave 0·4163 CO_2 and 0·1036 H_2O. C = 54·42; H = 5·52.
0·2052 ,, 0·4081 CO_2 ,, 0·1012 H_2O. C = 54·24; H = 5·48.
$C_{34}H_{41}O_{18}N$ requires C = 54·33; H = 5·46 per cent.

Tetra-acetyl-l-*mandelonitrile glucoside*, when recrystallised from alcohol, forms a mass of very fine, soft needles, which show parallel extinctions and are therefore orthorhombic:

0·2171 gave 0·4506 CO_2 and 0·1046 H_2O. C = 56·60; H = 5·36.
0·2055 ,, 0·4289 CO_2 ,, 0·1000 H_2O. C = 56·92; H = 5·41.
$C_{22}H_{25}O_{10}N$ requires C = 57·02; H = 5·40 per cent.

Tetra-acetylprulaurasin.—To prepare this compound, the crude material obtained by evaporating down an aqueous solution of the glucoside in a vacuum was dissolved in twenty times its weight of boiling acetic anhydride; after boiling the liquid during three hours, it was poured into water; an oil separated which solidified only after several days at a low temperature. The solidified acetyl compound dissolved with great readiness in benzene, chloroform, ethyl acetate, methyl acetate, acetone, or alcohol, but not in light petroleum. It could only be obtained crystalline by cooling a strong solution in alcohol to about − 5°; very small needles showing a parallel extinction were then obtained:

0·1907 gave 0·3988 CO_2 and 0·0886 H_2O. C = 57·03; H = 5·16.
$C_{22}H_{25}O_{10}N$ requires C = 57·02; H = 5·40 per cent.

Inasmuch as sambunigrin is probably a single substance like Fischer's glucoside, the fact that it occurs alone in certain plants whilst a mixture of the two isomeric glucosides is met with in others raises interesting questions. Benzylidene cyanohydrol, formed by the coalescence of benzaldehyde and hydrogen cyanide, being a mixture of stereoisomerides, it is rather to be expected that the two glucosides should occur together; from this point of view, prulaurasin is a normal product and the appearance of sambunigrin alone is somewhat remarkable; the latter is also a remarkable substance as it does not correspond to amygdalin and because no corresponding bioside is known. Amygdalin is not known to occur in leaves but only in the fruits and kernels; it is not improbable that its isomeride may be met with in the fruits of plants the leaves of which contain sambunigrin; it should have a higher lævorotatory power, $[\alpha]_D$ − 60°, approximately.

Our best thanks are due to Professor H. E. Armstrong for most valuable criticism and advice.

CHEMICAL DEPARTMENT,
CITY AND GUILDS OF LONDON INSTITUTE,
CENTRAL TECHNICAL COLLEGE, SOUTH KENSINGTON.

LXIII.—*The Interaction of Ammonium Salts and the Constituents of the Soil.*

By ALFRED DANIEL HALL, M.A., and CONRAD THEODORE GIMINGHAM.

IT has been observed that the application of neutral ammonium salts, such as the sulphate and the chloride, to soils has resulted in the production of an acid reaction. In the field this was first noticed on the experimental plots of the Royal Agricultural Society at Woburn, where the soil is sandy and deficient in calcium carbonate; the application of 200 lb. per acre of ammonium sulphate and chloride in mixture every year for about twenty-five years brought the soil into such an acid condition that it reddens blue litmus paper and will no longer allow of the growth of barley (see Voelcker, *J. Roy. Agric. Soc.*, 1899, **60**, 515, and 1901, **62**, 286). A similar acid reaction is found upon some of the permanent grass plots at Rothamsted, where still larger amounts of ammonium salts have been used for a longer period, but the arable plots at Rothamsted show no such acidity, because of the considerable proportion of calcium carbonate contained in their soil. From time to time various observers have noted an acid reaction produced in the laboratory when soil is treated with a neutral solution of an ammonium salt, but this is only true of a few soils, and is due to the formation and subsequent hydrolysis of ferric and aluminium salts (Veitch, *J. Amer. Chem. Soc.*, 1904, **26**, 637).

In the course of an investigation into some of the effects brought about by this acidity the action of dilute solutions of ammonium salts on the various constituents of a normal soil was examined in some detail and the present paper deals with that part of the work. The first examination of the action of ammonium salts on the soil is due to Way (*J. Roy. Agric. Soc.*, [i], **11**, 323; **13**, 123), who showed that a double decomposition takes place, ammonium being withdrawn from solution and an equivalent amount of calcium, magnesium, potassium, or sodium passing into solution. Other investigators (see A. Voelcker, *J. Roy. Agric. Soc.*, [i], 1860, **21**, 105; Warington, Trans., 1868, **21**; Van Bemmelen, *Zeitsch. physikal. Chem.*, 1895, **18**, 331; Armsby, *Amer. J. Sci.*, 1877, [iii], **14**, 75) have extended Way's observations and determined quantitative relations between the amounts of soil and the ammonium absorbed. In the general process by which the soil absorbs ammonium salts, none of which washes through the soil into the drainage water under normal conditions, there is also some reaction with the calcium carbonate in the soil with the production of ammonium carbonate and calcium salts, but the comparative magnitude of the two reactions with the clay and the calcium carbonate has remained doubtful.

The authors have not used soil in their investigations, but have taken its proximate constituents separately, namely, sand, clay, humus, and calcium carbonate. The trials with sand and with silica of various origin may be dismissed at once since no action could be detected. For the experiments with clay a fine modelling clay of a light grey colour was used, showing in the dry state the following composition:

Al_2O_3, 20·46; Fe_2O_3, 1·04; CaO, 0·20; MgO, 0·17; K_2O, 1·67; Na_2O, 1·03; SiO_2, 68·70; constitutional water, 5·57; moisture lost at 100°, 0·82; total 99·66.

It is clear that the clay contains a considerable proportion of finely-divided silica; the alumina present would only be equivalent to about 51 per cent. of kaolinite in the whole. It was dried and powdered, so that from the bulk an equal sample could be taken for each experiment. As a rule 100 grams of dry clay were placed in an Erlenmeyer flask with 300 c.c. of the solution of ammonium salt and the mixture shaken for twenty hours in an end-over-end revolving shaker. It was found that in this period of twenty hours the action was completed, indeed it probably takes place with considerable rapidity. After shaking, the mixture was filtered and an aliquot portion of the clear liquid taken for estimation of the ammonia by distillation with soda and titration.

The following facts were observed:

(1) No production of free acid could be detected; the reaction of the salt solution was determined, using *N*/100 acid or alkali and methyl-orange or phenolphthalein as indicators, both before and after shaking with the clay, but no change was found. As it seemed possible that free acid might arise through hydrolysis of the ammonium salt followed by evaporation of the ammonia, other experiments were tried in which the salt solution was allowed to evaporate spontaneously in contact with the clay, or was placed with the clay in a gas washing bottle through which a rapid stream of ammonia-free air was passed for three days, but in neither case was there a measurable development of free acid or any loss of ammonia.

In another experiment the air was replaced by carbon dioxide, but with a similar negative result.

(2) There is no withdrawal of the acid radicle from solution. Determinations were made of the chlorine in the solution before and after shaking with the clay, but no change could be estimated. Similarly, when ammonium sulphate was used determinations of the sulphuric acid in solution before and after shaking showed no withdrawal of sulphuric acid. This agrees with the observations of previous workers.

Since there is no change of reaction and no withdrawal of the acid radicle from solution, it follows that there is no "adsorption" or "laking out" of the salt as a whole, at any rate not in quantities appreciable by ordinary gravimetric methods. In another connexion in the Rothamsted laboratory measurements were made of the conductivity of very dilute solutions of ammonium salts before and after adding a small amount of clay; no change in the conductivity of the solution occurs such as would be found if an appreciable amount of the salt were withdrawn from solution.

It follows then that the reaction of the ammonium salts on the clay must be purely one of double decomposition, and by qualitative analysis calcium, magnesium, and potassium were found in the final solution.

In a quantitative experiment the following results were obtained on shaking up 300 grams of clay with 900 c.c. of $N/5$ ammonium chloride:

	Gram.	
NH_3 absorbed per 100 grams of clay	= 0·1200	
Ca in solution per 300 c.c.	= 0·0283	= 0·0481 gram of NH_3
Mg ,, ,,	= 0·0506	= 0·0717 ,, ,,
K ,, ,,	= 0·0076	= 0·0033 ,, ,,
		0·1231

No aluminium was found in solution. It will be seen that the calcium, magnesium, and potassium in solution were equivalent to the ammonium precipitated, sodium being present only in traces if at all.

Clay is a product of the weathering of various double silicates like the felspars, and although in the main it consists of kaolinite,

$$Al_2O_3,2SiO_2,2H_2O,$$

as the analysis shows, it still contains other bases which form, with the alumina, double hydrated silicates of a zeolitic nature. That the reaction is with zeolitic substances in the clay may be inferred from the following experiments, in which 50 grams of the clay, 50 grams of a washed kaolin, and 50 grams of natrolite (pure picked crystals ground fine) respectively, were shaken with 300 c.c. of $N/10$ solution of ammonium chloride:

	Gram NH_3 removed from solution.	NH_3 in solution.
Clay	0·073	0·437
Kaolin	0·051	0·459
Natrolite	0·061	0·449

The natrolite gives results intermediate between those of the clay and the kaolin and all three are of the same order. The compound formed by the introduction of ammonium into the clay molecule is a stable one, which does not yield up ammonium on washing with pure water, as has been stated.

It is seen that the absorption of the ammonium from the solution is by no means complete; although as much as 50 grams of clay were in contact with only 1·605 grams of ammonium chloride, in the position of equilibrium attained, there was six times as much ammonia in solution as was combined with the clay.

Further experiments were then made to ascertain the character of the reaction: in the first series the amount of clay was kept constant, and it was always present in large excess; the amount of water was also constant, the ammonium salt being the variable. The following results were obtained:

TABLE I.—*Reaction of* 100 *grams clay with* 300 *c.c. solution.*

Ammonium chloride.

Original concentration of NH_4Cl.	Gram NH_3 originally present in 300 c.c.	Gram NH_3 left in solution.	Gram NH_3 on solid.	Percentage removed.
N/10	0·51	0·384	0·126	24·7
N/12	0·408	0·293	0·115	28·1
N/15	0·34	0·236	0·104	30·5
N/20	0·255	0·165	0·090	35·3
N/30	0·17	0·102	0·068	40·26
N/50	0·102	0·053	0·049	48·0
N/100	0·051	0·020	0·031	60·0

Ammonium sulphate.

Concentration of $(NH_4)_2SO_4$.				
N/10	0·5082	0·3888	0·1194	23·5
N/12	0·4278	0·3234	0·1044	24·4
N/15	0·3474	0·2562	0·0912	26·25
N/20	0·2616	0·1812	0·0804	30·7
N/30	0·1686	0·1059	0·0627	37·2
N/50	0·1074	0·0603	0·0471	43·8
N/100	0·0521	0·0234	0·0287	55·1

These results can be expressed by an equation of the type,

$$\underset{a.}{2NH_4Cl} + \underset{b.}{Cax} \rightleftarrows \underset{c.}{2NH_4x} + \underset{d.}{CaCl_2}.$$

$$K \propto c^2/a.$$

Thus for strengths of ammonium chloride between *N*/10 and *N*/100 the mean value of K is 0·046, whilst for ammonium sulphate it becomes 0·0354.

The accompanying curves show a comparison between the experimental result and the calculated curve, using the mean values for K already given; the discrepancy between the result with *N*/10 ammonium chloride and the calculated position is due to the fact that about this point the clay ceases to combine with any further ammonium.

Other salts of ammonium were also tried, the carbonate and the phosphate, and as the results show when expressed in the curves,

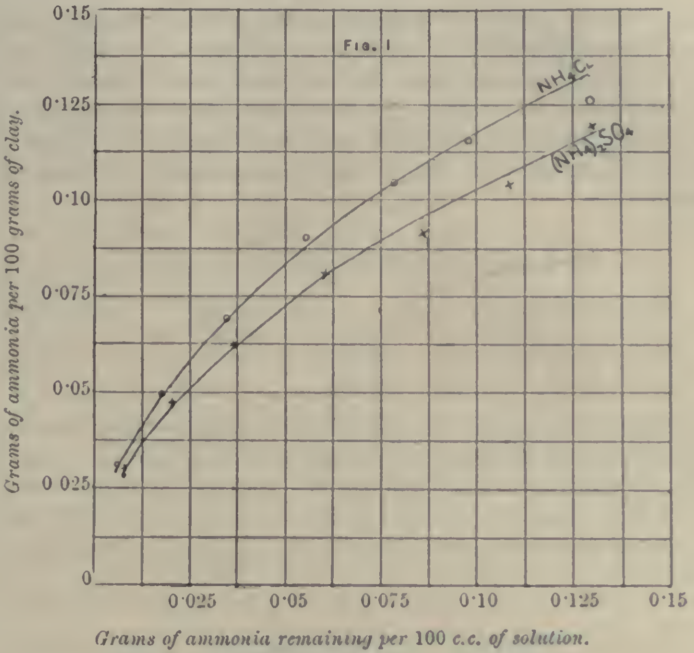
Fig. I
NH₄Cl
(NH₄)₂SO₄
0·15
0·125
0·10
0·075
0·05
0 025
0
0·025
0·05
0·075
0·10
0·125
0·15
Grams of ammonia per 100 grams of clay.
Grams of ammonia remaining per 100 c.c. of solution.

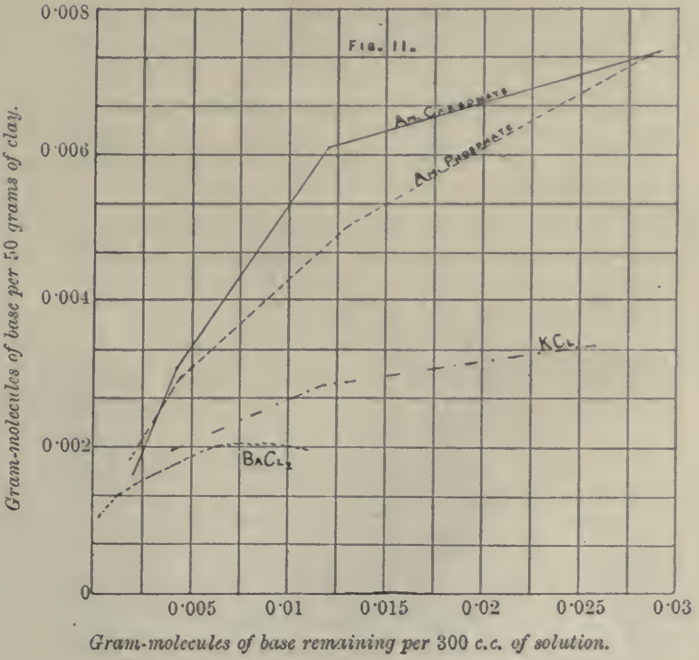
Fig. II.
Am. Carbonate
Am. Phosphate
KCl
BaCl₂
0·008
0·006
0·004
0·002
0
0·005
0·01
0·015
0·02
0·025
0·03
Gram-molecules of base per 50 grams of clay.
Gram-molecules of base remaining per 300 c.c. of solution.

Fig. 2, the reaction was of a similar nature, as also was the reaction with barium and potassium chlorides and hydrochloric acid. In the case of ammonium phosphate and carbonate some of the acid was also removed from solution, as would naturally be the case through the formation of insoluble salts of calcium and magnesium. Determinations are given below for the amount of phosphoric acid going out of solution :

Fifty grams clay shaken with 300 *c.c. solution.*

Strength of solution.	After shaking.	Percentage of P_2O_5 withdrawn.
5·22 grams P_2O_5 per litre	4·73 grams P_2O_5 per litre	9·4
1·044 ,, ,,	0·901 ,, ,,	13·7
0·522 ,, ,,	0·423 ,, ,,	18·96

Attempts were made to determine the absorption of ammonium hydroxide, but failed owing to difficulties of manipulation. The clay became deflocculated and would not settle from the mixture even when left to stand for months, for the same reason it could not be filtered, and attempts to bring about a separation by centrifuging also failed.

TABLE II.—*Reaction of* 50 *grams clay with* 300 *c.c. solution.*

Concentration of Am. phosphate.	Gram NH_3 originally present in 300 c.c.	Gram NH_3 left in solution.	Gram NH_3 on solid.
N/10	0·51	0·407	0·103
N/20	0·255	0·1846	0·0704
N/50	0·102	0·061	0·041
N/100	0·051	0·026	0·025
Concentration of Am. carbonate.			
N/10	0·51	0·406	0·104
N/20	0·255	0·169	0·086
N/50	0·102	0·059	0·043
N/100	0·051	0·023	0·023
Concentration of $BaCl_2$.	Grams Ba originally present in 300 c.c.	Grams Ba left in solution.	Gram Ba on solid.
	1·747	1·483	0·264
	1·164	0·882	0·282
	0·873	0·632	0·241
	0·349	0·165	0·184
	0·175	0·038	0·137
Concentration of KCl.	Grams K originally present in 300 c.c.	Grams K left in solution.	Gram K on solid.
	1·1367	1·0053	0·1314
	0·5688	0·4604	0·1084
	0·2274	0·055	0·0724

TABLE II.—*Reaction of* 50 *grams clay with* 300 *c.c. solution* (continued).

Concentration of HCl.	Gram H originally present in 300 c.c.	Gram H left in solution.	Gram H on solid.
N/10	0·03	0·0258	0·0042
N/20	0·015	0·01146	0·00354
N/50	0·006	0·0037	0·0023

In all the above cases the clay was present in large excess; when the ammonium salts are in excess the reaction proceeds until a definite point is reached and then stops, so that a given weight of clay removes the same amount of ammonium from solution whatever the strength of the solution of ammonium salt with which it is in contact.

It is difficult to attain a satisfactory degree of accuracy in the experiments bearing on this point; it is impossible to remove the clay by filtration and wash it free from the adhering liquid, because as soon as the salts in the latter have been reduced below a certain point the clay becomes deflocculated and begins to pass through the filter paper. When, again, the concentration of the solution in ammonium is determined before and after shaking with the clay, as in the previous experiments, and the ammonium withdrawn by the clay determined by difference, we have to deal with large quantities of ammonium and all the errors in their estimation are multiplied and thrown on the small difference which is the quantity sought. This method, however, had to be followed: the solutions were made up by weight and the quantities weighed, and other precautions were taken to ensure accuracy, but still the figures sought, the ammonium withdrawn from solution by 100 grams of clay, are not in very close agreement, although sufficiently so to indicate the nature of the reaction.

The following table shows the results of shaking 900 c.c. of *N*/5, *N*/10, and *N*/20 ammonium chloride solution with 225, 150, 60, and 30 grams of clay respectively:

TABLE III.—*Reaction of clay with ammonium chloride in excess.*

Grams clay.	Grams NH_4Cl solution.	Grams NH_3 in original solution.	Grams NH_3 in solution at end.	Gram NH_3 removed by clay.	Gram NH_3 removed by 100 grams clay.	
		N/5 Series.				
125	504·48	1·7067	1·5373	0·1694	0·136	mean 0·147
83·33	504·15	1·7057	1·5582	0·1475	0·177	
60	907·45	3·0701	2·9925	0·0776	0·129	
		N/10 Series.				
225	905·35	1·5409	1·2401	0·3008	0·133	mean 0·148
150	903·70	1·5376	1·2842	0·2534	0·169	
60	905·58	1·5408	1·4560	0·0848	0·141	

TABLE III.—*Reaction of clay with ammonium chloride in excess* (continued).

Grams clay.	Grams NH_4Cl solution.	Gram NH_3 in original solution.	Gram NH_3 in solution at end.	Gram NH_3 removed by clay.	Gram NH_3 removed by 100 grams clay.
			N/20 Series.		
125	500·7	0·4275	0·3106	0·1169	0·094
83·33	502·32	0·4289	0·3370	0·0919	0·110
60	903·3	0·7713	0·7029	0·0684	0·114
30	904·17	0·7721	0·7311	0·0410	0·137

It will be seen that when varying quantities of clay were shaken with N/5 and *N*/10 solutions of ammonium chloride, 100 grams of clay withdrew approximately 0·147 gram of ammonium from solution, whatever the quantity of solution with which it was in contact. With the *N*/20 solution, and particularly with the large amounts of clay, the mass of the clay began to exercise a sensible influence on the result, and the amount of ammonium withdrawn per 100 grams of clay fell.

Only when the amount of clay was reduced to 30 grams in contact with 900 c.c. of *N*/20 ammonium chloride did the amount of ammonium withdrawn per 100 grams of clay approximate to the amount withdrawn when the clay was in contact with the stronger solutions.

The particular limit of saturation for the ammonium on the clay indicated in these experiments, 0·147 gram per 100 grams of clay, was found to vary with each sample of clay employed. Even variations in the drying process, through which portions of the stock material were put, altered the limit, so that it is necessary to prepare at one time a sufficient quantity to carry through the whole series. The clay used in the latter experiments is thus not strictly comparable with the clay used in the previous series, although they were originally two samples from a common stock.

Effect of Calcium Carbonate.

Since the share taken by calcium carbonate in the absorption of ammonium salts by soil is still doubtful, the authors made some determinations by shaking up 300 c.c. of similar ammonium sulphate solutions with 50 grams of powdered calcium carbonate. The results showed that an equilibrium reaction of the type:

$$(NH_4)_2SO_4 + CaCO_3 \rightleftharpoons (NH_4)_2CO_3 + CaSO_4,$$

takes place, and that only a small proportion of the ammonium sulphate changes into carbonate, even when the calcium carbonate is present in large excess.

A fuller series of experiments made with 200 c.c. of solutions of ammonium chloride and 20 grams of finely-divided calcium carbonate (a precipitate obtained in a hard-water softening process on a large scale) gave the following results. Preliminary trials showed that the reaction was complete in the twenty-four hours allowed for shaking:

TABLE IV.—20 *Grams of calcium carbonate and* 200 *c.c. of ammonium chloride solution.*

NH_3 present (grams per 200 c.c.).	CaO finally in solution (gram per 200 c.c.).	NH_3 equivalent to Ca dissolved (gram per 200 c.c.).
3·398	0·0506	0·0308
2·832	0·0442	0·0268
2·269	0·0428	0·0261
1·700	0·0348	0·0211
0·680	0·0240	0·0145
0·340	0·0162	0·00982
0·17	0·0110	0·0066

These figures conform to an equation of the type:

$$K \propto \frac{(CaCl_2)^2}{NH_4Cl},$$

which is of the same type as the reaction with clay.

These experiments do not agree with the statements of Way (*loc. cit.*) and Knop (*Boniterung der Ackereide*, 1871, 49), who maintain that calcium carbonate is without action on the ammonium salts.

When ammonium chloride solutions were shaken with a mixture of 50 grams of clay and 10 grams of calcium carbonate, the total precipitation of ammonium was somewhat increased, but the type of the reaction remained unchanged, as shown by the results below:

TABLE V.

Gram NH_4 per 300 c.c.	Gram NH_4 taken up by 50 grams clay alone.	Gram NH_4 taken up by 50 grams clay + 10 grams $CaCO_3$.
0·51	0·073	0·084
0·255	0·057	0·069
0·102	0·034	0·036

Since few soils would contain as much as 10 grams of calcium carbonate per 50 grams of clay, it may be concluded that the main reaction when ammonium salts are applied to the soil takes place with the clay, although the calcium carbonate will afterwards continue to decompose the zeolitic ammonium compound as ammonium carbonate is removed by nitrification. It has been shown (Hall and Miller, *Proc. Roy. Soc.*, 1905, *B*, 77, 1) that the ultimate result of applying ammonium salts to the soil is the removal of an approximately equivalent amount of calcium carbonate, although Ashby (*Jour. Agric. Science*, 1907, 2) found that the zeolitic ammonium compound can be nitrified without further base.

Experiments with Humus.

The action of clay on ammonium salts having failed to give rise to any acid reaction, a similar series of trials was made with humus in place of clay.

Three samples of peat were employed:

(1) A sandy peat such as is used for orchid growing, consisting mainly of the debris of bracken not greatly decomposed.

(2) A loose sphagnum peat commonly sold as peat moss litter, still showing considerable vegetable structure.

(3) A solid black Irish peat from some depth, with no visible vegetable structure.

Qualitative tests for the production of acidity were also made with the decayed peaty grass residues which are to be found on the surface of some of the Rothamsted grass plots where the acid reaction of the soil is most in evidence, and with the loose friable humus obtained from the interior of a hollow tree. In all cases the peat was first washed repeatedly with hot distilled water, although its acid reaction could never be entirely removed.

The first tests showed that there was no production of acidity when any of these samples of humus were shaken up with the solutions of ammonium salts. Determinations were made of the acidity of distilled water and of the ammonium salt solutions after shaking with equal weights of the same peat; the acidity was barely measurable, but was less with the salt solutions than with pure water. Ammonium had, however, been removed from solution, hence some base must have been dissolved from the peat to maintain a neutral reaction. Qualitative tests showed this base to be calcium, and analysis of the peat ash showed the presence in the dry (No. 3) peat of 1·2 per cent. of CaO. It is concluded that the peat contains this calcium combined as humate, and that the reaction with ammonium salts consists in a double decomposition between the calcium humate and the ammonium salt.

The absorption of ammonium was then determined in the same way as with clay, after shaking 300 c.c. of the solution of the salt with 25 grams of peat. The following results show the reaction to be of a similar type to that with clay:

25 *Grams peat moss litter with* 300 *c.c.* NH_4Cl *solution.*

Strength of solution taken.	NH_3 in 300 c.c. originally.	NH_3 left in solution.	NH_3 on peat.
N/10	0·51	0·458	0·052
N/20	0·255	0·221	0·034
N/100	0·051	0·0424	0·0086

A further 50 grams of peat were then extracted with hydrochloric acid for forty-eight hours and repeatedly washed with hot distilled water to remove acid as far as possible. The residue was then shaken with *N*/10 ammonium chloride as before. After filtering, the solutions showed an acid reaction and ammonium had been withdrawn from solution, but the acidity was small, and some of the precipitated ammonium had been replaced by calcium, small quantities of which could be detected in solution, despite the digestion with strong acid to which the peat had been previously subjected. It seems, however, certain that free "humic acid" can to some extent decompose ammonium salts with the formation of an insoluble ammonium compound, and this is confirmed by the observation that whereas the humus, after all mineral acid had been washed away, yielded a brown solution on shaking with pure water, when shaken with the ammonium salt a colourless solution resulted.

As free "humic acid" does not appear to be a normal constituent of soils, this experiment does not vitiate the general conclusion reached by the authors that the constituents of the soil do not react with solutions of ammonium salts to produce a free acid. For the acid observed in the field experiments quoted a biological origin has now been found.

THE ROTHAMSTED EXPERIMENTAL STATION,
LAWES AGRICULTURAL TRUST.

LXIV.—*The Reduction of Carbon Dioxide to Formaldehyde in Aqueous Solution.*

By HENRY JOHN HORSTMAN FENTON.

THE reduction of carbon dioxide in aqueous solution has always formed an attractive subject for investigation, not only from a purely chemical standpoint, but also from its important bearing on the problem of assimilation in plants. Interest in this question has recently received a fresh stimulus owing to the extremely suggestive summary of the subject which was given in the President's address at the last annual meeting of the Society. The practical demonstration of this reduction, by purely chemical methods, has been the object of a very large number of interesting researches, and, since the time when Baeyer first suggested his well-known hypothesis of carbon dioxide assimilation, one of the principal aims of these investigations has been the recognition of formaldehyde as a reduction product. If one excepts the somewhat inconclusive and yet unconfirmed experiment of Bach, in which palladium-hydrogen was employed as the reducer, to which attention will presently be drawn, it would appear that in no single case has formaldehyde been detected. This statement refers, of course, to the reduction in aqueous solution; that formaldehyde can indirectly result as a reduction product of gaseous carbon dioxide in presence of moisture, under the influence of the silent discharge, appears to have been established by Löb (*Zeitsch. Elektrochem.*, 1905, **11**, 745, and 1906, **12**, 282).

Maly, in 1865 (*Annalen*, **135**, 119), acted on a concentrated solution of ammonium carbonate with dilute (liquid) sodium amalgam and showed that after acidification and distillation of the product a notable quantity of formic acid was obtained in the distillate.

Lieben (*Monatsch.*, 1895, **16**, 211, and 1897, **18**, 582) extended this observation and made an exhaustive investigation of the reduction of carbonates, or carbon dioxide in presence of various metallic salts, by different metals. He found that when a slow stream of carbon dioxide was passed for some weeks through water to which, from time to time, small quantities of sodium amalgam were added, considerable quantities of formate could be obtained, and similar results were given by amalgams of barium or potassium. Aluminium amalgam alone did not reduce a solution of carbon dioxide, but in presence of sodium sulphate, sodium phosphate, or some other salts, good yields of formate resulted. When magnesium or platinised magnesium were used, alone or in presence of salts, under conditions which in the case of the other metals were found to be most favourable, the results were entirely negative, or at most traces only of formate were obtained. In his second paper, the author draws particular attention to this peculiarity of magnesium, and ascribes the results to the difference in the amount of energy set free in the liberation of hydrogen by the metals. Ballo (*Ber.*, 1884, **17**, 6) also prepared formates by reduction of bicarbonates with sodium or potassium, but with platinised magnesium only negative results were obtained.

The reduction of carbon dioxide in aqueous solution by the electrolytic method was first effected by Royer (*Compt. rend.*, 1870, **70**, 731), the solution being subjected to what the author termed the "intra-pilaire" current in a Grove or Bunsen cell. In this case again formic acid was the only product of reduction.

Coehn and Jahn (*Ber.*, 1904, **37**, 2836) made an extended study of the electrolytic reduction, and investigated the behaviour of different salts and the influence due to the nature of the cathode metal. The best results were obtained when a cold saturated solution of potassium sulphate was electrolysed, using an amalgamated zinc cathode, and a continuous current of carbon dioxide was conducted through the solution. In this way the alkali formed at the cathode was at once converted into bicarbonate. In order to examine the nature of the reduction product the anodic and cathodic solutions, which during electrolysis were separated by a porous cell, were mixed together and the acidity of the mixture determined after removal of the carbon dioxide in a current of air. An aliquot part of the solution was also titrated with permanganate, and the results, calculated as formic acid, usually agreed with the values calculated from the acidity. But in some experiments the oxidation values were higher than the acidity values, a circumstance which appeared to indicate a reduction product other than formic acid. No formaldehyde, however, could be detected.

Reduction was not obtained when normal carbonates were similarly electrolysed, and carbon dioxide, in presence of strong acids, also gave negative results, although an aqueous solution of carbon dioxide alone gave rise to formic acid, as in Royer's experiment. The authors therefore concluded that neither the CO_3 ion nor the non-dissociated carbonic acid is reducible, and that formic acid results from the reduction of the HCO_3 ion.

Ehrenfeld, however (*Ber.*, 1905, **38**, 4138), shows that formate is also produced by the electrolytic reduction of a strongly ammoniacal solution of ammonium carbonate and considers that in this case the ion NH_4CO_3 is reduced.

In all the above-named investigations the authors come to the conclusion that formic acid is the sole product of the reduction of carbon dioxide; in no case could formaldehyde be discovered.

The photo-reduction of carbon dioxide in presence of uranyl acetate was said by Bach (*Compt. rend.*, 1893, **116**, 1145) to give rise to formaldehyde, and Usher and Priestley (*Proc. Roy. Soc.*, 1906, **77**, 370) state that they have confirmed this result. The method of proof, however, is not given. Moreover, the last named authors have since shown (*loc. cit.*, **78**, 322) that no formaldehyde can be detected if uranyl sulphate is substituted for the acetate, and, as regards the precipitation of uranium hydroxides, Euler has shown that a similar result is obtained when nitrogen is substituted for the carbon dioxide

(*Ber.*, 1904, **37**, 3415). The supposed formation of formaldehyde when dimethylaniline was used as catalyser, in place of the uranyl salt, has also been disproved by Euler (*loc. cit.*, 3416); compare also Pilhashy (*J. Amer. Chem. Soc.*, 1900, **22**, 132). Bach has also stated (*Compt. rend.*, 1898, **126**, 479) that formaldehyde is produced when a solution of carbon dioxide is reduced by hydrogen-palladium; the nature of his experiment and the method of proof will be gathered from the following statement. Ten grams of spongy palladium and 2·85 grams of palladium foil were charged with hydrogen and introduced into water which had been boiled and cooled in a stream of carbon dioxide. Carbon dioxide was passed into the mixture for three days and the solution was filtered after thirty days. The addition of aqueous aniline gave "un faible dépôt blanc," which, from its appearance when crystallised and its melting point, was considered to be methylene-aniline. The melting point of the product is not stated. Another portion of the liquid when evaporated to dryness with excess of ammonia left a residue which, when dissolved in a little water, gave a yellow precipitate with bromine water.

EXPERIMENTAL.

Since it has been established by the various authors referred to in the foregoing summary that carbon dioxide is readily reduced, in various ways, to formic acid, it appeared interesting to attempt the further reduction of formic acid to formaldehyde. If this attempt were successful the practical demonstration of the reduction of carbon dioxide to formaldehyde would be complete. The systematic and direct reduction of acids to corresponding aldehydes has hitherto succeeded only in the case of hydroxy-acids which can yield lactones, the lactone, in fact, being the product which undergoes reduction (Fischer, *Ber.*, 1889, **22**, 2204, and 1890, **23**, 930). It was altogether improbable therefore that the desired object, in the present case, would be attained by the use of sodium. But, in the course of a series of experiments with other reducing agents, it was found that metallic magnesium readily reduces formic acid to formaldehyde.

When a rod of magnesium was introduced into a solution of pure formic acid (about 10 per cent.) a vigorous reaction ensued and the solution, after some minutes, showed strongly-marked reactions of formaldehyde with the colour tests mentioned below. After the action had proceeded for about half an hour the solution, when neutralised with sodium carbonate and boiled, gave off a strong odour of the aldehyde. In order to complete the identification of the product, a few drops of phenylhydrazine acetate were added, and the resulting nearly white precipitate was washed with water, a little alcohol, and ether, and was then recrystallised from a mixture of absolute alcohol and toluene. The product so obtained crystallised in lustrous, white plates which melted at 184—185° (compare Wallace Walker, Trans., 1896, **69**, 1278). With hydrogen sulphide the solution gave, on standing, a bulky, white, crystalline precipitate; aqueous aniline gave a white precipitate, and ammoniacal silver nitrate was reduced in the cold.

The yield of formaldehyde, estimated by Romijn's iodine method, amounted to about 1 to 2 per cent. of the formic acid used; the greater part of the acid is of course rendered inert, as regards reduction, by conversion into magnesium formate. By suitable treatment with acids and regulation of the temperature and concentration, it would doubtless be possible to obtain very much larger yields. Ammonium formate, in solution, reacts violently with metallic magnesium; a large quantity of ammonia is evolved, and the solution after a few minutes gives, strongly, the reactions of formaldehyde. If the resulting solution is evaporated to dryness on a water-bath and the residue extracted with chloroform, notable quantities of hexamethylenetetramine are obtained and can be identified in the manner indicated below.

The results obtained, therefore, show that carbon dioxide can be reduced to formaldehyde with formic acid as the intermediate stage. But it still remained a matter of interest to ascertain whether the complete reduction could be demonstrated in one operation. This again is found to be possible with the aid of metallic magnesium, if certain conditions are employed. In this case there is no evidence that the formic acid stage is passed through, and, judging from the results of Lieben and of Ballo, the occurrence of this stage would appear to be improbable.

When a stream of carbon dioxide is passed to saturation for about eighteen to twenty-four hours through pure water in contact with several rods of amalgamated magnesium, the solution obtained gives slight but unmistakable indications of formaldehyde with the colour tests to be mentioned. It was afterwards found that if small quantities of ammonia, aniline, phenylhydrazine, or piperidine are first added to the water, the indications of formaldehyde are much more marked; aluminium hydroxide, ferric hydroxide, and calcium carbonate all show a similar influence, especially if the mixtures are warmed. Ammonia and phenylhydrazine appear to give the best results, and in presence of either of these reagents it is easy to demonstrate the production of formaldehyde even after a few minutes. An aqueous solution of phenylhydrazine, for example, when mixed with excess of magnesium powder and subjected to a rapid stream of carbon dioxide, allowing the temperature to rise to 60—70°, gives, after about ten minutes, an intense blue colour with test No. I (see p. 693). Aniline gives similar results; in this case and with phenylhydrazine the solutions begin to precipitate on standing for some time. The products, however, are very likely impure, since phenylhydrazine probably undergoes some reduction to aniline and ammonia, and methyleneaniline, as shown by Miller and Plöchl (*Ber.*, 1902, **25**, 2020), is easily reducible to methylaniline.

When ammonia or ammonium carbonate is used in contact with amalgamated magnesium rods, or more rapidly with magnesium powder, the product gives, after acidification in the cold, only slight indications of formaldehyde, but if the mixture is heated to boiling after acidification, the reactions are strongly marked. The aldehyde is in fact "fixed," as fast as formed, as hexamethylenetetramine. If the ammoniacal solution is evaporated * just to dryness, and the residue extracted with chloroform, a small quantity of crystalline residue is obtained, from the chloroform solution, which is easily recognised as hexamethylenetetramine by Legler's method (*Ber.*, 1885, **18**, 3350: compare also Horton, *ibid.*, 1888, **21**, 1999). When exposed to the vapours of bromine it swells and turns dark brick-red; on exposure to air bromine is evolved, and a sulphur-yellow powder is left. These products are the tetra- and di-bromides respectively. The aqueous solution gives, with bromine water, a yellow precipitate. Silver nitrate gives a white precipitate which dissolves and is reduced to a mirror on heating, and iodine in aqueous-alcoholic solution gives a dark reddish-brown, crystalline precipitate.

It was noticed in some experiments that on heating the mixture obtained by the action of carbon dioxide on magnesium in presence of ammonium carbonate with caustic soda there appeared at some stage of the operation a distinct "fishy" odour of the methylamines. This result is to be expected since hexamethylenetetramine, as shown by Delépine (*Bull. Soc. Chim.*, 1895, [iii], **13**, 135), can be reduced by zinc to trimethylamine. The formation of mono-, di-, and tri-methylamines from formaldehyde and ammonia, and from hexamethylenetetramine, has also been shown by other authors (compare Eschweiler, *Ber.*, 1905, **38**, 880; Ischidzu and Inouye, *Jour. Pharm. Soc. Japan*, Jan. 1, 1906, &c.).

The latter observation appears to be of interest in connexion with the fact that trimethylamine is of frequent occurrence in certain plants and also as regards the close relationship of this substance to betaine.

The quantities of formaldehyde, or its derivatives, which are obtained in the manner above indicated are of necessity only small. The actual mass of carbon dioxide available for reduction in solution is limited, of course, by the small solubility of the gas at the temperature employed. The best results are obtained when the gas is "rushed" through the solution at a rapid rate, since, so far, no convenient apparatus has been available for working under increased pressure. Further, the magnesium rapidly loses its activity, probably owing to a superficial coating of basic carbonate, and attempts to remedy this by addition of mineral acids yield only negative results. When the magnesium is used in the form of powder it appears to be advantageous first to saturate the solution with magnesium bicarbonate; this moderates, to some extent, the over-rapid action of the metal and probably increases the potential concentration of the carbon dioxide (or HCO_3 ions) at the temperature employed (compare Rinne, *Chem. Zeit.*, 1907, 31, 125).

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* Since a considerable loss of the product occurs when the solution is completely evaporated at 100°, it is best to finish the evaporation in a vacuum desiccator at the ordinary temperature.

In the course of the foregoing investigation a considerable number of the well-known tests for formaldehyde have been compared and studied. In the authors' opinion the following three are the most delicate and most satisfactory of the colour-reactions, and to these preference is given in the order named.

I. To the solution to be examined is added a few drops each of dilute solutions of phenylhydrazine hydrochloride, sodium nitroprusside, and caustic soda; the result is a bright but transient Prussian-blue colour (Rimini's test).

II. The solution is mixed with a few drops of an alcoholic solution of gallic acid, and the mixture is carefully poured on to pure concentrated sulphuric acid; a bright blue ring appears where the liquids meet.

III. An aqueous solution of resorcinol is substituted for the alcoholic gallic acid in II; the result is a red or reddish-violet ring (compare Mulliken, *Identification of Carbon Compounds*, p. 24).

The conditions of formation of formaldehyde from carbon dioxide and the behaviour of metallic magnesium towards other acids are being further studied. Acetic acid gives recognisable quantities of acetaldehyde when treated with magnesium, but negative results have so far been obtained with propionic and *n*-butyric acids.

LXV.—*An Extension of the Benzoin Synthesis.*

By Reginald W. L. Clarke and Arthur Lapworth.

The observation that benzaldehyde is readily converted into benzoin by means of potassium cyanide was first made by Zinin (*Annalen*, 1840, **31**, 329 and **34**, 186), although the details of the method as at present usually practised were suggested by Zincke (*ibid.*, 1879, **198**, 151), whilst Fischer extended it to the condensation of furfuraldehyde.

The reaction is of especial interest, first, because the potassium cyanide plays the part of a true catalytic agent, being practically unaltered in amount at the end of the operation and need be used only in relatively small quantities, and secondly, because it is one which is not applicable to the aldehydes of the fatty series.

Of the theories which have been put forward as to the mechanism of the reaction may first be mentioned those of Zincke (*Ber.*, 1876, **9**, 1772), Pomeranz (*Monatsh.*, 1900, **21**, 389), Koelichen (*Zeitsch. physikal. Chem.*, 1900, **33**, 129), and Nef (*Annalen*, 1895, **287**, 342, and 1897, **298**, 312).

Zincke assumed that mandelonitrile was formed as an intermediate product and that this, reacting with unchanged benzaldehyde, with elimination of hydrogen cyanide, yielded benzoin; but he found that benzaldehyde and hydrocyanic acid did not react to give benzoin. Pomeranz assumed a catalytic action of hydroxyl ions and Nef supposed the change to be similar in character to an aldol condensation.

The theory of Chalanoy and Knoevenagel is well known (*Ber.*, 1892, **25**, 295). They suggested that a potassium derivative of benzaldehyde and mandelonitrile was formed in the first instance and these subsequently reacted in the following manner,

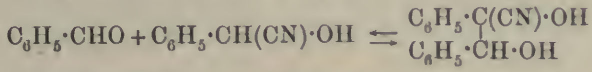
$$C_6H_5\cdot CK{:}O + C_6H_5\cdot CH(OH)\cdot CN = C_6H_5\cdot CH(OH)\cdot CO\cdot C_6H_5 + KCN,$$

but the existence of this potassium compound was purely hypothetical, for no compound of this kind has been isolated, nor is there even any indirect evidence that the hydrogen atom assumed to be replaced by potassium is reactive in presence of alkalis.

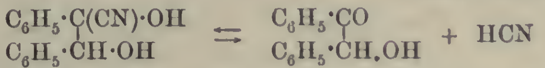
In a series of papers on the additive reactions of hydrogen cyanide, one of the present authors showed that the addition of this compound to aldehydes and ketones is dependent on the presence of cyanogen ions, and suggested that a complex cyanogen ion is formed at an intermediate stage in all cases (Trans., 1903, **83**, 995; 1904, **85**, 1206). Thus in the case of benzaldehyde the complex ion $C_6H_5\cdot CH{<}^{O'}_{CN}$ was assumed to be formed in the first instance. It was further shown that benzaldehyde yields mandelonitrile with potassium cyanide even in presence of alkali (Trans., 1903, **83**, 1003), and the benzoin reaction was attributed to a reaction of benzaldehyde with mandelonitrile. The latter, being a hydroxybenzyl cyanide, contains a reactive hydrogen attached to the carbon atom between the phenyl group and the cyano-group, and in virtue of this must be capable of forming an aldol-like condensation product with aldehydes. With benzaldehyde, the product must be the unstable cyanohydrin of benzoin (*loc. cit.*, 1004). The following thus represents the suggested stages in the reaction :

$$C_6H_5\cdot CHO + CN' \rightleftharpoons C_6H_5\cdot CH(CN)\cdot O' \quad . \; . \; . \; . \; . \; . \; . \quad \text{I.}$$

$$C_6H_5\cdot CH(CN)\cdot O' + \dot{H} \rightleftharpoons C_6H_5\cdot CH(CN)\cdot OH \quad . \; . \; . \; . \; . \; . \quad \text{II.}$$



$$C_6H_5\cdot CHO + C_6H_5\cdot CH(CN)\cdot OH \rightleftharpoons \begin{array}{l} C_6H_5\cdot C(CN)\cdot OH \\ C_6H_5\cdot CH\cdot OH \end{array} \quad . \; . \; . \quad \text{III.}$$



$$\begin{array}{l} C_6H_5\cdot C(CN)\cdot OH \\ C_6H_5\cdot CH\cdot OH \end{array} \rightleftharpoons \begin{array}{l} C_6H_5\cdot CO \\ C_6H_5\cdot CH.OH \end{array} + HCN \quad . \; . \; . \; . \quad \text{IV.}$$

This scheme serves to explain (1) why cyanide is necessary, because, although there is no evidence that the hydrogen atom in the $\cdot CH{:}O$ group of aldehydes higher than formaldehyde is reactive in presence of bases, it is well recognised that in the $\cdot CH$ group between $CN\cdot$ and an$\cdot$ aromatic nucleus, the hydrogen atom is labile and the occurrence of an aldol-like reaction between benzaldehyde and benzyl cyanide in presence of alkalis is no longer in doubt ; (2) the need for the use of potassium cyanide instead of hydrogen cyanide alone because reactions I and III do not occur with measurable speed in absence of bases ; (3) aliphatic aldehydes do not react in the same way as does benzaldehyde, because the fatty nitriles with the group $\begin{matrix} C \\ C \end{matrix}\!\!>CH\cdot CN$ or $C\cdot CH_2\cdot CN$ manifest relatively very little tendency to take part in the aldol and allied condensations, in comparison with those of the aromatic series.

Finally, reactions III and IV belong to well-known types, whilst direct evidence of the existence of the complex ion assumed in I and II was obtained later, when an additive compound of benzaldehyde and potassium cyanide (the potassium derivative of mandelonitrile) $C_6H_5\cdot CH(CN)\cdot OK$ was isolated (Trans., 1904, **85**, 1208).

Some time after these suggestions were published, a communication from Bredig and Stern appeared (*Zeitsch. Elektrochem.*, 1904, **10**, 582, *et seq.*). They described experiments on the velocity of the benzoin condensation and were able fully to establish that the reaction is brought about catalytically by the potassium cyanide, the velocity being directly proportional to the concentration of the cyanogen ion in all cases. They accepted the view that a complex ion is formed as in I above, but as they found that the velocity was not affected by the addition of excess of a base, they assumed that the change subsequent to I was as follows:

$$C_6H_5\cdot CH\!<\!\begin{matrix}O'\\CN\end{matrix} + C_6H_5\cdot CHO = C_6H_5\cdot CH(OH)\cdot CO\cdot C_6H_5 + CN' \quad . \quad . \quad \text{V.}$$

A further reason for rejecting the view expressed by III was advanced by one of these authors (Stern, *Inaugural Dissertation*, Leipzig, 1904, p. 39), namely, that above 25° the amount of the intermediate products present is extremely minute ("bei höherer Temperatur als 25° die Menge der eventuellen Zwischenproducte äusserst gering ist"), a conclusion drawn from conductivity experiments on solutions of benzaldehyde and potassium cyanide at varying temperatures.

It must here be pointed out, however, that the dependence of III on the concentration of hydroxyl ions is not more inevitable than that suggested by Bredig and Stern, nor can the second objection be sustained as conclusive. This depends on a variety of unknown circumstances and in particular on the ultimate mechanism of the aldol condensation III, which itself must be regarded as a complicated change.

If, for example, III proceeds as the result of a preliminary ionisation of mandelonitrile at the :CH· group, followed by a union of the resulting ion with benzaldehyde in this way:

$$\dot{H} + C_6H_5\cdot C'(CN)\cdot OH + C_6H_5\cdot CHO = \dot{H} + \begin{array}{l} C_6H_5\cdot C(CN)\cdot OH \\ C_6H_5\cdot CH\cdot O' \end{array} = \begin{array}{l} C_6H_5\cdot C(CN)\cdot OH \\ C_6H_5\cdot CH\cdot OH \end{array},$$

then the velocity will be proportional to the concentration of this new ion, and therefore to that of the isomeric ion as in the theory of Bredig and Stern, if the simple ion reactions

$$\dot{H} + C_6H_5\cdot CH(CN)\cdot O' \longleftrightarrow C_6H_5\cdot CH(CN)\cdot OH \longleftrightarrow C_6H_5\cdot C'(CN)\cdot OH + \dot{H}$$

are relatively very large, as would almost certainly be the case.

If, in accordance with Lapworth's view, mandelonitrile unites with benzaldehyde to form, in the first instance, an aldol-like product, namely, benzoincyanohydrin, in virtue of the presence of the labile hydrogen atom in the group :CH·CN, then it is to be anticipated that the nitrile will be found capable of taking part in other condensations in which substances yielding aldols in this way play a part.

One of the most familiar reactions of such compounds is that in which they unite with $\alpha\beta$-unsaturated ketones, &c., in accordance with the equation (where X = ·CO·, ·CN, &c.).

$$X\cdot\underset{\cdot}{\dot{C}}H + \underset{\cdot}{\dot{C}}{:}\dot{C}\cdot\dot{C}O = X\cdot\underset{\cdot}{\dot{C}}\cdot\dot{C}\cdot\dot{C}H\cdot\dot{C}O.$$

Mandelonitrile might thus be expected to react with $\alpha\beta$-unsaturated ketones as follows:

$$C_6H_5\cdot CH(CN)\cdot OH + \dot{\underset{\cdot}{C}}:\dot{\underset{\cdot}{C}}\cdot\dot{C}O = HO\cdot(CN)C(C_6H_5)\cdot\dot{\underset{\cdot}{C}}\cdot\dot{C}H\cdot\dot{C}O,$$

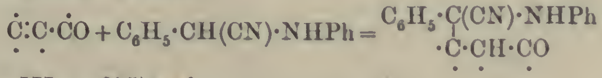
that is, yielding the cyanohydrin of a δ-diketone,

$$CO(C_6H_5)\cdot\dot{\underset{\cdot}{C}}\cdot\dot{C}H\cdot\dot{C}O,$$

which the product might at once give by elimination of hydrogen cyanide, as in the benzoin condensation itself.

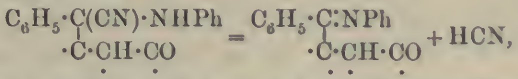
On making experiments in this direction with mandelonitrile it was found that the latter was too unstable and that the products of its decomposition took part in by-reactions which obscured the result of the condensation and similar results attended the use of the benzoyl derivative of mandelonitrile. It was therefore decided to employ a derivative of the nitrile less easily affected by alkalis, but of exactly analogous structure, and for this purpose the aniline derivative, namely, the compound obtained by combining hydrogen cyanide with benzylideneaniline, $C_6H_5\cdot CH(CN)\cdot NH\cdot C_6H_5$, was used.

Comparing the expected reactions of this compound with the reaction III and IV respectively, supposed to obtain during the benzoin reaction, we have



$$\dot{\underset{\cdot}{C}}:\underset{\cdot}{C}\cdot\dot{C}O + C_6H_5\cdot CH(CN)\cdot NHPh = \begin{array}{l} C_6H_5\cdot C(CN)\cdot NHPh \\ \qquad\cdot\underset{\cdot}{C}\cdot\underset{\cdot}{C}H\cdot\underset{\cdot}{C}O \end{array}$$

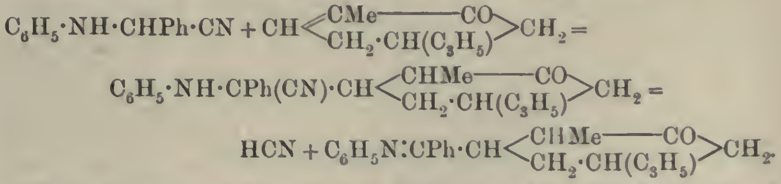
(compare III, p. 695) and



$$\begin{array}{l} C_6H_5\cdot C(CN)\cdot NHPh \\ \qquad\cdot\underset{\cdot}{C}\cdot CH\cdot\underset{\cdot}{C}O \end{array} = \begin{array}{l} C_6H_5\cdot C:NPh \\ \qquad\cdot\underset{\cdot}{C}\cdot\underset{\cdot}{C}H\cdot\underset{\cdot}{C}O \end{array} + HCN,$$

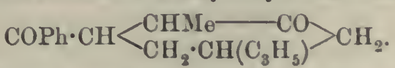
(compare IV, *loc. cit.*), that is to say, the phenylimino-derivative of the β-benzoyldihydroketone would finally be obtained.

On trying the reaction with carvone as the unsaturated ketone it was found to occur in exactly the manner anticipated, the phenylimino-derivative of β-benzoyldihydrocarvone being produced.



$$C_6H_5\cdot NH\cdot CHPh\cdot CN + CH{<}\begin{array}{l} CMe\text{———}CO \\ CH_2\cdot CH(C_3H_5) \end{array}{>}CH_2 =$$
$$C_6H_5\cdot NH\cdot CPh(CN)\cdot CH{<}\begin{array}{l} CHMe\text{——}CO \\ CH_2\cdot CH(C_3H_5) \end{array}{>}CH_2 =$$
$$HCN + C_6H_5N:CPh\cdot CH{<}\begin{array}{l} CHMe\text{——}CO \\ CH_2\cdot CH(C_3H_5) \end{array}{>}CH_2.$$

The new substance is easily hydrolysed by acids with formation of aniline and two stereoisomeric benzoyldihydrocarvones,



$$COPh\cdot CH{<}\begin{array}{l} CHMe\text{——}CO \\ CH_2\cdot CH(C_3H_5) \end{array}{>}CH_2.$$

One of these is present in preponderating amount, and has the properties which should attach to a substance having the structure here assigned to it. Thus, it absorbs only one molecular proportion of bromine, showing that it now contains only the carbon double linking in the *iso*propenyl group. It shows the phenomenon of mutarotation in presence of traces of alkalis indicating that it contains the group $\frac{X}{Y}{>}CH{\cdot}CO{\cdot}$, not present in the original carvone. Further, although it could be made to unite with only one molecular proportion of hydroxylamine, its dioxime was finally isolated by the indirect process of treating the original phenylimino-compound with hydroxylamine acetate, aniline being eliminated in the process.

A by-product obtained during the condensation of benzylideneaniline hydrocyanide with carvone is worthy of brief notice here. It has the composition of a compound of benzylideneaniline and benzylideneaniline hydrocyanide united in molecular proportions, and is almost certainly formed by a reaction again precisely analogous to the benzoin condensation proper, its formation being represented as follows,

$$NPh{:}CHPh + CHPh(CN){\cdot}NHPh = NHPh{\cdot}CHPh{\cdot}CPh(CN){\cdot}NHPh,$$

when it is formulated as benzoincyanohydrin, in which the hydroxyl groups are replaced by aniline residues.

The above synthesis of the anil of benzoyldihydrocarvone appears to confirm the view that mandelonitrile is in reality an intermediate product in the benzoin synthesis, but at the same time it suggests an analogy with the hypothetical condensation as expressed by Bredig and Stern (given on p. 696), for in both a cyanogen ion is eliminated and the product thus found without cyanogen. It was therefore thought very desirable that other cases of the condensation of benzylideneaniline hydrocyanide with $\alpha\beta$-unsaturated ketones should be investigated in the expectation that the intermediate cyano-compound corresponding to that postulated by Lapworth might be sufficiently stable to be isolated.

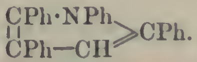
This hope was realised when, instead of carvone, benzylideneacetophenone was used. The interaction of the latter and benzylideneaniline hydrocyanide takes place very rapidly in dilute alcoholic solution, and if the proper conditions are employed the product separates at once on addition of a little alkali to the mixed solution, and the reaction takes place in the following manner:

$$COPh{\cdot}CH{:}CHPh + CHPh(CN){\cdot}NHPh = COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CPh(CN){\cdot}NHPh.$$

This substance, the analogue of benzoincyanohydrin, retains its hydrogen cyanide with remarkable tenacity, but, when heated above its melting point, loses the elements of hydrogen cyanide and of water. This is easily understood, as elimination of hydrogen cyanide would lead to the formation of the aniline derivative of an open chain δ-diketone (in this instance of desylacetophenone),

$$NPh{:}CPh\cdot CHPh\cdot CH_2\cdot COPh,$$

but these compounds very readily pass, with loss of water, into substituted pyrroles, and the product here should therefore yield tetraphenylpyrrole,



$$\left.\begin{matrix}CPh\cdot NPh\\ \|\\ CPh{-}CH\end{matrix}\right>CPh.$$

On examination the product was, in fact, found to be identical with the substance having the structure depicted, obtained by Smith (Trans., 1890, **57**, 646) on heating desylacetophenone with aniline.

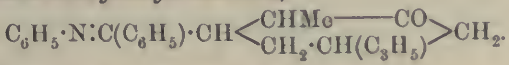
It is worthy of note that the original process for preparing this compound from benzaldehyde involved (1) the benzoin condensation, (2) the interaction of the product and acetophenone, and (3) the action of aniline on the compound so obtained. In the present case the same reactions are used, but in a different order, the benzoin condensation being brought about in a manner which throws definite light on the changes involved therein.

It should be mentioned that benzylideneaniline itself does not yield the condensation products described in this paper, the presence of cyanide and alkali being essential in both instances as in the benzoin condensation proper.

EXPERIMENTAL.

Condensation of Benzylideneaniline Hydrocyanide with Carvone.

β-Phenyliminobenzoyldihydrocarvone,



$$C_6H_5\cdot N{:}C(C_6H_5)\cdot CH\left<\begin{matrix}CHMe\text{——}CO\\ CH_2\cdot CH(C_3H_5)\end{matrix}\right>CH_2.$$

Preliminary experiments having shown that mandelonitrile was too readily decomposed by alkali to form condensation products with αβ-unsaturated ketones, its aniline derivative was prepared by shaking a cold alcoholic solution of benzylideneaniline with the requisite quantity of hydrogen cyanide in presence of potassium cyanide, a method which gives a nearly quantitative yield of the hydrocyanide.

Twenty-two grams of this substance were mixed with 15 grams of carvone and an equal bulk of alcohol, and the whole warmed until a clear solution was formed. On cooling rapidly to 25°, and before the hydrocyanide had commenced to separate, 12 c.c. of a 50 per cent. solution of potassium hydroxide were added; the whole was cooled in a stream of water and allowed to remain with occasional shaking for some hours. Water was then added to the pasty product, the insoluble material being collected and washed free from alkali. When dry, the nearly solid mass was extracted with cold carbon disulphide, which was separated by decantation and mixed with one and a half times its bulk of light petroleum in order to precipitate unchanged benzylideneaniline hydrocyanide. The filtered solution was evaporated to about two-thirds of its original bulk and allowed to cool. Large transparent rhombs of the condensation product slowly separated and were collected and recrystallised twice from alcohol. On analysis:

0·2012 gave 0·6126 CO_2 and 0·1392 H_2O. C = 83·0; H = 7·7.
0·1998 ,, 0·6090 CO_2 ,, 0·1363 H_2O. C = 83·1; H = 7·6.
0·1918 ,, 7·0 c.c. moist nitrogen at 15° and 765 mm. N = 4·3.
$C_{23}H_{25}ON$ requires C = 83·4; H = 7·6; N = 4·2 per cent.

The molecular weight of the compound in benzene solution was determined by the cryoscopic method. The addition of 0·5063 gram of the substance to 16·68 grams of benzene caused a depression in the freezing point of 0·47°, and a subsequent addition of 0·4173 gram of the substance produced a further depression of 0·375°. The molecular weight as indicated in these experiments was 323 and 333 respectively, that calculated for a compound having the formula $C_{23}H_{25}ON$ being 331.

β-Phenyliminobenzoyldihydrocarvone is slightly soluble in light petroleum and dissolves very readily in alcohol, ether, benzene, carbon disulphide, or chloroform. It crystallises from alcohol or carbon disulphide in large, transparent, pale yellow rhombs which melt at 98·5—100°. The crystals are biaxial in character, the axial angle being wide and the double refraction strong.

For the determination of the rotatory power, 0·2500 gram dissolved and made up to 25 c.c. with absolute alcohol was examined in a 2-dcm. tube at 17°. The rotation observed was − 7·38°, whence $[\alpha]_D - 369{\cdot}0$.

The substance decomposes slowly at the ordinary temperature, and specimens which have been crystallised from alcohol deteriorate more rapidly than those obtained from solution in carbon disulphide. In a few months the material is converted into a viscid, transparent oil which did not crystallise. The change may be brought about rapidly by warming the compound on the water-bath.

The substance unites directly with hydrocyanic acid in presence of bases, but does not yield a well-defined semicarbazone or phenylhydrazone. With hydroxylamine, it gives an oxime of the corresponding diketone, aniline being eliminated.

The *cyanohydrin*, $C_{23}H_{25}ON,HCN$, was prepared by dissolving the foregoing phenylimine in alcohol, adding the calculated quantity of potassium cyanide dissolved in a small quantity of water, and then acidifying with acetic acid drop by drop. The crystalline material which separated was collected, washed, and dried.

The substance could only be crystallised from chloroform, and the crystals which separated contained chloroform of crystallisation. It was not found possible to expel this by heat:

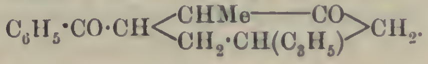
0·2102 gave 0·1243 AgCl. $CHCl_3 = 16·4$.

0·5607 „ 31·9 c.c. moist nitrogen at 14° and 759 mm. N (calculated for the chloroform-free substance) = 8·0.

$C_{23}H_{25}ON,HCN$ requires N = 7·8 per cent.

The compound crystallised in minute, colourless, slender, silky needles, readily soluble in chloroform, less readily so in alcohol, ether, acetone, or carbon disulphide, and sparingly so in light petroleum.

Formation of Isomeric β-Benzoyldihydrocarvones,



$$C_6H_5\cdot CO\cdot CH{<}\begin{matrix}CHMe\text{——}CO\\CH_2\cdot CH(C_3H_5)\end{matrix}{>}CH_2.$$

The phenylimino-compound is readily hydrolysed by dilute mineral acids, and the following method furnishes a good yield of the corresponding diketone. The substance is covered with five times its weight of aqueous hydrochloric acid and warmed on the water-bath. The yellow crystals, at first, in part dissolve, but after a few minutes the clear solution becomes turbid and an oil separates; this increases in amount until all the crystals have disappeared. At the end of half an hour, the liquid is cooled, the oil collected, washed with water, and triturated with a little alcohol. A few crystals separate and the amount of these rapidly increases if a few drops of sodium hydroxide solution are added. The solid matter is then separated from the residual oil by filtration and purified by repeated crystallisation from hot alcohol:

0·2038 gave 0·5945 CO_2 and 0·1442 H_2O. C = 79·6; H = 7·9.

$C_{17}H_{20}O_2$ requires C = 79·70; H = 7·8 per cent.

The new compound dissolves readily in most of the ordinary media, with the exception of light petroleum, and separates from hot alcohol in crystals which melt at 117—118°.

The crystals are irregular, opaque plates with pectinate edges, and the optical properties could not be distinguished. After fusion between glass slips the substance solidifies rapidly just below its melting point to patches of transparent plates and few air spaces; in convergent polarised light some of these plates show a biaxial figure of small angle. The double refraction is positive in sign and weak.

For the determination of the optical activity, 0·2500 dissolved and made up to 25·1 c.c. with absolute alcohol at 18° was examined in a 2-dcm. tube.

The rotation observed was constant at $-1·01°$, whence $[\alpha]_D$ $-50·7$, but when a trace of sodium ethoxide was added, the rotation decreased until at the end of a few hours it attained the value $-0{\cdot}80°$ at 18°, corresponding with $[\alpha]_D$ $-40{\cdot}2$.

This change in rotatory power indicates the probable existence of stereoisomeric forms of the ketone, and this explains the effect of alkali on the crude, oily ketone. An isomeride was obtained from the mother liquor from which the ordinary variety had been isolated. This was deposited in prismatic needles which were separated mechanically from the pectinate crystals of the first modification, and were recrystallised from alcohol. On analysis:

0·1934 gave 0·5653 CO_2 and 0·1349 H_2O. C = 79·7; H = 7·7.
$C_{17}H_{20}O_2$ requires C = 79·7; H = 7·8 per cent.

The crystals melt at 84—86°, but further investigation of this compound was not possible, owing to the small quantity available.

The ordinary form of the diketone behaves as an unsaturated compound and at once discharges the colour of solutions of bromine in sodium acetate, or of potassium permanganate.

In order to determine how many ethylenic linkings were present, 1 gram of the substance was dissolved in acetic acid to which excess of sodium acetate was added, and then titrated with a standard solution of bromine in the same solvent; the amount of bromine absorbed was 0·645 gram, hence 1 gram-molecule of the ketone requires 165 grams or 2 atoms of bromine, indicating the presence of one ethylenic linking. The product was an oil.

The *cyanohydrin* was prepared by adding hydrochloric acid to a solution containing the diketone and excess of potassium cyanide in dilute alcohol. On dilution with water, an oil was precipitated which slowly solidified and was purified by crystallisation from a mixture of benzene and light petroleum:

0·2053 gave 8·8 c.c. moist nitrogen at 17° and 759 mm. N = 5·0.
$C_{17}H_{20}O_2$,HCN requires N = 4·9 per cent.

The compound dissolves freely in the usual organic media, with the exception of light petroleum, and separates from solution in rosettes of plates which sintered at 115° and melted at 117—118°.

The crystals, when examined in convergent polarized light, show, occasionally, the bisectrix of a figure of moderate angle emerging nearly normally to the field. The double refraction is negative.

The *semicarbazide* was prepared by warming the diketone with dilute alcoholic semicarbazine acetate for some hours, and was isolated by diluting the liquid, removing the precipitated matter, and crystallising from acetone. The crystals contained acetone of crystallisation, which was determined by heating some of the substance at 100° until it was constant in weight. 0·1423 lost 0·0214 acetone, or 15·0 per cent.

The nitrogen in another portion of the same specimen of the substance was determined:

0·1431 gave 14·1 c.c. moist nitrogen at 17° and 756 mm. N = 13·4.*

$C_{17}H_{20}O\colon N_2H\cdot CO\cdot NH_2$ requires N = 13·4 per cent.

The semicarbazone is sparingly soluble in most of the ordinary organic solvents, and separates from acetone in crystals which, when heated rapidly, fuse at 89°, evolving acetone with effervescence. The acetone-free substance melted at 170—173°.

The *dioxime*, $C_{17}H_{20}(N\cdot OH)_2$, was obtained by heating the anil for some hours on the water-bath with a solution of three molecular proportions of free hydroxylamine in dilute alcohol; on cooling, a solid separated which was crystallised from dilute alcohol:

0·1232 gave 0·3183 CO_2 and 0·0874 H_2O. C = 70·5; H = 7·9.
0·3321 „ 27·3 c.c. moist nitrogen at 14·5° and 765·5 mm. N = 9·7.

$C_{17}H_{22}O_2N_2$ requires C = 71·3; H = 7·7; N = 9·8 per cent.

The analysis indicates that aniline has been removed, and no difficulty was found in detecting aniline in the mother liquor by any of the ordinary tests.

The *dioxime* dissolves readily in hot alcohol and separates on cooling in slender, white needles melting at 138—139°.

Examination of the By-product obtained during the Preparation of Phenyliminobenzoyldihydrocarvone.

When a mixture of the hydrocyanide of benzylideneaniline and carvone was shaken with strong alkali, a sparingly soluble substance was always formed in considerable amount and was separated from the mass by means of carbon disulphide, in which it is insoluble.

It was purified by dissolving it fractionally with benzene in a Soxhlet extractor, and was finally obtained as a silky, homogeneous mass of needles:

0·2067 gave 0·6296 CO_2 and 0·1116 H_2O. C = 83·1; H = 6·0.
0·0778 „ 7·45 c.c. moist nitrogen at 15° and 747 mm. N = 11·0.

$C_{27}H_{23}N_3$ requires C = 83·3; H = 5·9; N = 10·8 per cent.

The substance is sparingly soluble in alcohol, chloroform, or acetone, and separates from hot benzene, in which it dissolves somewhat more freely, in crystals melting at 210—211°. When it is heated above its melting point, pungent aromatic fumes are evolved.

It is decomposed by hot alcoholic potassium hydroxide, yielding potassium cyanide; the liquid thus obtained, in one instance, was allowed to evaporate, when a solid was deposited which, when recrystallised from alcohol, separated in nacreous leaflets melting at 54°. This substance was hydrolysed by acid, giving benzaldehyde and aniline, and was proved to be benzylideneaniline, by the mixed melting point method; no other compound was obtained.

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* Calculated on acetone-free substance.

The by-product is thus formed by the union of two molecules of benzylideneaniline with one molecule of hydrogen cyanide:

$$C_{27}H_{23}N_3 = 2C_{13}H_{11}N + HCN.$$

Condensation of Benzylideneaniline Hydrocyanide with Benzylideneacetophenone.

γ-Cyano-α-benzoyl-γ-anilino-βγ-diphenylpropane,

$$C_6H_5\cdot CO\cdot CH_2\cdot CH(C_6H_5)\cdot C(C_6H_5)(CN)\cdot NH\cdot C_6H_5.$$

Equimolecular proportions of benzylideneacetophenone and benzylideneaniline hydrocyanide were dissolved separately in hot alcohol, the solutions were mixed and cooled rapidly to 35°, when a few drops of a 50 per cent. solution of potassium hydroxide were added, and the whole allowed to remain at the ordinary temperature until the crystalline substance which separated no longer increased in amount. The product was collected, washed with alcohol, and then with water, and was finally crystallised from boiling alcohol:

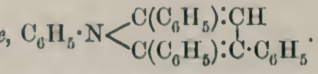
0·1994 gave 0·6095 CO_2 and 0·1040 H_2O. C = 83·4; H = 5·8.

$C_{29}H_{24}ON_2$ requires C = 83·7; H = 5·8 per cent.

The compound is somewhat sparingly soluble in alcohol, ethyl acetate, or acetone, and nearly insoluble in benzene, chloroform, or light petroleum. It separates from alcohol in small, glistening needles, which melt and decompose at 200°.

The crystals under the microscope are seen to be flat needles or elongated rectangular plates, having nearly a straight extinction in polarised light. Further optical characters could not be determined owing to the small size of the forms. When warmed with strong alcoholic potash the substance is in part decomposed, the odour of acetophenone may be distinguished, and the mother liquor, on treatment with ferrous sulphate, ferric chloride, and hydrochloric acid, gives a precipitate of Prussian blue.

Tetraphenylpyrrole,



$$C_6H_5\cdot N\Big<\begin{matrix}C(C_6H_5){:}CH\\ \quad\ \ |\\ C(C_6H_5){:}C\cdot C_6H_5\end{matrix}.$$

A few grams of the preceding compound were heated in a flask over a flame until effervescence was visible, and the temperature was then maintained about this point until further action ceased; steam and hydrogen cyanide were easily recognised to be the main gaseous products. The residue, which solidified on cooling, was purified by crystallisation from hot glacial acetic acid :

0·2022 gave 0·6685 CO_2 and 0·1044 H_2O. C = 90·2 ; H = 5·7.

$C_{28}H_{21}N$ requires C = 90·6 ; H = 5·7 per cent.

The compound melted at 197°, and further examination showed that its properties were identical in all respects with those of tetraphenylpyrrole, obtained by the action of aniline on desylacetophenone (Smith, Trans., 1890, **57**, 646).

The authors desire to express their indebtedness to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the cost of this investigation.

CHEMICAL DEPARTMENT,
GOLDSMITHS' COLLEGE,
NEW CROSS, S.E.

LXVI.—*Studies in Optical Superposition. Part III.*

By THOMAS STEWART PATTERSON and JOHN KAYE.

IN a recent paper (Trans., 1906, **89**, 1884) we described the preparation and optical behaviour of *l*-menthyl *l*-tartrate and its diacetyl derivative. We also gave reasons for supposing that van't Hoff's assumption regarding the summation of the rotations of several asymmetric atoms in one molecule is incorrect, and that, on the contrary, if, in a molecule which contains several asymmetric centres, the grouping about one of these be inverted, the corresponding change in the rotation may not be arrived at merely by altering the sign of the part of the total rotation due to that particular centre.

This conclusion was definitely expressed a number of years ago by Gadamer, whose work we have only recently had an opportunity of consulting. Gadamer (*Arch. Pharm.*, 1899, **237**, 92) prepared *d-sec*-butylthiocarbimide from *Cochleria officinalis*, and this compound on heating with water yielded *dd*-dibutylthiocarbamide, which was found to have a molecular rotation of + 77·08° at 17° in 3·3 per cent. solution in alcohol.

By the action of *dl-sec*-butylamine on *d-sec*-butylthiocarbimide a *dr*-dibutylthiocarbamide was obtained the molecular rotation of which under the same conditions was + 34·84°, distinctly less than half that of the compound in which both butyl groups were dextrorotatory. Amplifying this in a later paper (*Arch. Pharm.*, 1901, **239**, 290), he says : "Fande eine einfache Addition der beiden optischen Effecte statt, so müsste für den *dd*-Dibutylthioharnstoff $[M]_D$ dass Doppelte von den für *dr*-Dibutylthioharnstoff gefundenen Werte betragen, also 69·68°; statt dessen finden wir $[M]_D = 77·08°$, also rund ein Zehntel mehr." The point is referred to again in a paper by Urban (at Gadamer's suggestion), who gives data for butylcarbamides and butylthiocarbamides in alcohol and chloroform solutions, and arrives at the conclusion: "Die Regel dass die optischen Wirkungen zweier asymmetrischen Kohlenstoffatome im Molekül sich summieren, bestätigte sich nicht" (*Arch. Pharm.*, 1904, **242**, 85).

It appears to us, however, that this conclusion is not justified by the evidence, for it is clear that the compound which Gadamer names *dr*-dibutylthiocarbamide must consist of a mixture of molecules of *dd*-dibutylthiocarbamide and *dl*-dibutylthiocarbamide. Now the latter must be inactive, and therefore the principle of optical superposition is not really involved here, since the only comparison is between the rotation of pure *dd*-dibutylthiocarbamide on the one hand and of *dd*-dibutylthiocarbamide mixed with an inactive substance on the other. Gadamer, suggesting an alternative explanation of the fact that the rotation in the latter case is not exactly half of that in the former, says: "Allerdings ist dabei auf die Molekulargrösse noch keine Rücksicht genommen. Es ist vielleicht nicht ausgeschlossen dass dem *dr*-dibutylthioharnstoff als echte racemische Verbindung die doppelte Molekulargrösse zukommt und dadurch die beobachtete Verschiedenheit zu erklären ist" (*Arch. Pharm.*, 1901, **239**, 290). This suggestion, although not impossible, seems to us improbable, since, so far as we are aware, racemic substances always dissociate in dilute solution into a mixture of the *d*- and *l*-isomerides. A much more likely explanation of the experimental numbers is that *d*-butylthiocarbimide, when acted on by *dl-sec*-butylamine combines preferentially with the *l*-isomeride, so that the resulting product contains a greater number of molecules of *dl*-dibutylthiocarbamide than of *dd*-dibutylthiocarbamide, in which case the rotation of the mixture would necessarily be less than half that of the pure active compound.

We are thus of opinion that Gadamer's results do not supply data whereby the question of optical superposition can be crucially tested. In our last communication we showed that this can best be done by comparing the specific or molecular rotations of sets of compounds, such, for instance, as *l*-menthyl *d*-tartrate, *l*-menthyl *l*-tartrate, and *l*-menthyl *i*-tartrate or their acetyl derivatives. If the rotation of the *i*-compounds be found equal to the mean of the rotations of the *d*- and *l*-compounds, van't Hoff's assumption is proved for those cases at least. If, on the other hand, the values found differ to an extent distinctly beyond the experimental error, van't Hoff's assumption must be regarded as disproved.

Our present communication gives data for the rotation of *l*-menthyl diacetyl-*i*-tartrate in the homogeneous condition as well as in solution in ethyl alcohol, benzene, and nitrobenzene, and, as is shown further on, these data, taken in conjunction with the others previously published, furnish, for the first time, conclusive evidence as to the untenability of van't Hoff's assumption regarding optical superposition.

Di-l-*menthyl* i-*tartrate* was prepared by mixing 10 grams of *i*-tartaric acid with 50 grams of menthol and passing dry hydrogen chloride through the mixture, first in the cold and then at a temperature of 110—130° for about twenty hours. The excess of menthol was then distilled off under reduced pressure. The viscid oil which remained was dissolved in ethyl alcohol and boiled with animal charcoal for two hours. On addition of water to the filtered solution the tartrate was precipitated as an oil, but although various methods were tried it did not crystallise. It was therefore converted directly into the diacetyl derivative.

Di-l-*menthyl diacetyl*-i-*tartrate* was readily obtained by boiling the menthyl tartrate with acetyl chloride. The solid which remained after the excess of acetyl chloride had been distilled off was washed with water and sodium carbonate solution and crystallised twice from methyl alcohol. The melting point was 129°, which is higher than that of either the corresponding *d*- (108°) or *l*- (102·5°) compound, although the melting point of *i*-tartaric acid (143°) is lower than that of *d*- or *l*-tartaric acid (172°). On analysis:

0·2186 gave 0·5272 CO_2 and 0·1746 H_2O. C = 65·77 ; H = 8·87.

$C_{28}H_{46}O_8$ requires C = 65·88 ; H = 9·02 per cent.

The composition of the ester was further verified by decomposing 0·3435 gram of the substance with 20 c.c. of 0·4021*N*-ethyl-alcoholic potassium hydroxide solution. To neutralise the excess of alkali 14·6 c.c. of 0·3656 *N*-hydrochloric acid were necessary. Therefore 6·72 c.c. of the alkali had been utilised for saponification whilst theory requires 6·70 c.c.

When melted the ester was slightly opalescent, and as this greatly interfered with polarimetric measurements the preparation was boiled in ethereal solution with animal charcoal for four hours, and was then twice crystallised from absolute ethyl alcohol. The melting point was the same as before. The compound, thus purified, was then examined in the polarimeter with the following results, but owing to the readiness with which the ester solidifies on cooling, it was not found possible to obtain values for the rotation at such low temperatures as in the cases of the *d*- and *l*-compounds:

Rotation of l-*Menthyl Diacetyl*-i-*tartrate.*

t°.	$\alpha_D^{t^\circ}$ (30 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
145·6°	−15·888°	0·9540	−55·52°	−283·1°
122·6	16·145	0·9751	55·20	281·5
140·0	15·954	0·9592	55·44	282·7
130·1	16·060	0·9683	55·29	282·0
100·0 *	—	—	54·88 *	280·0 *
20·0 *	—	—	53·7 *	274·0 *

Densities determined:

Temperature.........	134°	139·6°	150·6°	161·4°
Density...............	0·9636	0·9596	0·9495	0·9395

* Extrapolated.

The results recorded in the first part of this investigation wer obtained with an instrument which did not easily allow of observations at temperatures above 100°. Our rotation data for *l*-menthyl diacetyl-*d*-tartrate would therefore require to be extrapolated in order to allow of comparison with those given above, or vice versa. We therefore thought it worth while to re-examine *l*-menthyl diacetyl-*d*-tartrate at higher temperatures so that our data should be as definite as possible.* The values found were as follows:

Rotation of l-*Menthyl Diacetyl*-d-*tartrate.*

t°.	$\alpha_D^{t^\circ}$ (30 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
97·2°	−13·345°	0·9970	−44·63°	−227·6°
123·3	12·467	0·9758	42·59	217·2
134·4	12·171	0·9668	41·96	214·0

These numbers agree very closely with the values previously obtained. The molecular rotation formerly determined at 99·2° was −227·2°, which, allowing for the slight diminution of rotation due to rise of temperature, is practically identical with the number given above for 97·2°.

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* We have also redetermined the density of this substance. Two series of observations were made with different pyknometers, the results being as follows:

Temperature	113°	134·5°	119°	146·5°
Density	0·9835	0·9660	0·9801	0·9577

These values agree closely with each other, but differ slightly from those given in Trans., 1905, **87**, 40. All the rotation data for *l*-menthyl diacetyl-*d*-tartrate in the present paper are calculated by means of the new density determinations. This redetermination also affects the numbers for *l*-menthyl diacetyl-*d*-tartrate quoted in Trans., 1906, **89**, 1897, but the necessary changes, which are small, do not affect the argument in any way.

Rotation of l-*Menthyl Diacetyl*-i-*tartrate in Solution.*

Solution in Ethyl Alcohol (d. 20°/4° : 0·7915).

The ester is but slightly soluble in ethyl alcohol, and it was therefore only possible to examine a dilute solution.

p : 0·4547.

t°.	$\alpha_D^{t^\circ}$ (400 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
16·6°	−0·827°	0·7954	−57·2°	−291°
35·5	0·828	0·7784	58·5	298
20·0 *	—	—	57·3 *	292 *

Densities determined :

Temperature	18·53°	23·2°
Density	0·79368	0·78964

Solution in Benzene (d. 20°/4° : 0·87749).

p : 5·20404.

t°.	$\alpha_D^{t^\circ}$ (100 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
17·2°	−2·225°	0·8885	−48·12°	−245·4°
30·3	2·250	0·8746	49·43	252·1
37·7	2·291	0·8668	50·79	259·0
50·5	2·314	0·8535	52·10	265·7
20·0 *	—	—	48·59 *	247·8 *

Densities determined :

Temperature	19°	23°	28·8°
Density	0·88641	0·88233	0·87617

* Interpolated.

Solution in Nitrobenzene (d. 20°/4° : 1·20328).

p : 4·378.

t°.	$\alpha_D^{t^\circ}$ (100 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]^{t^\circ}$.
17·2°	−2·504°	1·1984	−47·73°	−243·4°
27·6	2·514	1·1883	48·32	246·4
37·4	2·574	1·1787	49·88	254·3
20 *	—	—	47·81 *	243·8 *

Densities determined :

Temperature	19·85°	22·1°	34·8°
Density	1·19603	1·19385	1·18158

* Interpolated.

Discussion of Results.

We may now consider these data in connexion with the corresponding values for the dextro- and lævo-compounds. The following table exhibits this comparison at different temperatures for the homogeneous substances :

Molecular Rotation of l-*Menthyl Diacetyl*-d-*tartrate*, l-*Menthyl Diacetyl*-l-*tartrate and* l-*Menthyl Diacetyl*-i-*tartrate.*

t°	I. *l*-Menthyl diacetyl-*d*-tartrate.	II. *l*-Menthyl diacetyl-*l*-tartrate.	III. Mean of I and II.	IV. *l*-Menthyl diacetyl-*i*-tartrate.	Δ. IV—III.
20°	−255°	−360°	−307·5°	−274°	33·5°
100	226	382	304	280	24
130	215	390	302·5	282	20·5

In order to obtain a value for the molecular rotation of the *i*-tartrate at 20° extrapolation through 100° is necessary, and therefore the number given is subject to error. The values at 100° and 130° are more trustworthy, especially the latter, since it is found by interpolation. The values for the *d*- and *l*-esters are all interpolated.

It will be observed that at all three temperatures the molecular rotation of the *i*-tartrate is very distinctly—almost 10 per cent.—greater (that is, less negative) than the mean of the values for the *d*- and *l*-esters. This difference is greatest at low temperatures, so that the influence of rise of temperature, in this as in many other similar cases, is to diminish those forces which, acting between the atoms of a molecule, are evidenced by absence of additive regularities in the properties of the substance. The properties—rotation in this case—become more nearly additive at higher temperatures than they are at lower ones.

Solutions.—The next table gives a comparison of the values of molecular rotation which we have found for these esters in solution at 20°. The numbers given for the *d*- and *l*-tartrates are interpolated values for p : 5 solutions. Those for the *i*-tartrate are as stated. The slight difference in concentration of the benzene and nitrobenzene solutions would have no appreciable influence on the relationship, and this is also the case for the somewhat greater difference of concentration in ethyl alcohol.

Solvent.	I. *l*-Menthyl diacetyl-*d*-tartrate.	II. *l*-Menthyl diacetyl-*l*-tartrate.	III. Mean of I and II.	IV. *l*-Menthyl diacetyl-*i*-tartrate.	Δ. IV—III.
Ethyl alcohol......	−268°	−367°	−317·5°	−292° (*p* : 0·455)	25·5°
Benzene	285	313	299	248 (*p* : 5·2)	51
Nitrobenzene	238	355	296·5	244 (*p* : 4·38)	52·5

It is apparent from these data that in solution also, as in the homogeneous state, the values for the rotation of the *i*-tartrate differ quite markedly—almost as much as 25 per cent.—from the means of the values for the *d*- and *l*-tartrates, and therefore that van't Hoff's conjecture regarding the summation of the rotations due to the different asymmetric carbon atoms in a compound containing several is incorrect.

The proof given is, we think, quite conclusive, since the differences upon which it depends are in all cases well beyond the limits of the experimental error, and the work is free from objections such as we have discussed in the previous part of this investigation.

It is of interest to compare our results with some obtained by Walden (*Zeitsch. physikal. Chem.*, 1896, **20**, 377), which have been referred to by us already (Trans., 1906, **89**, 1887).

His figures are:

	$[M]_D^{20°}$.
Di-*l*-amyl *i*-tartrate	+13·83°
Di-*l*-amyl *dl*-tartrate	9·77

The rotation of di-*l*-amyl *dl*-tartrate should represent the mean of the rotations of di-*l*-amyl *d*-tartrate and di-*l*-amyl *l*-tartrate if it consisted—which is somewhat doubtful—of equal numbers of these molecules. It will be observed that the rotation of the *i*-tartrate is greater than that of the *dl*-tartrate, and the same relationship occurs in all our results; the rotation of the *i*-compound is always greater (less negative) than the mean value for the *d*- and *l*-derivatives, and therefore we must conclude that the rotation due to a given asymmetric atom in a compound of two or more asymmetric radicles is not independent of the configuration of the other group or groups with which it is combined.

It gives us pleasure, in conclusion, to acknowledge our indebtedness to the Research Fund Committee of the Chemical Society for a grant which defrayed the expenses of this investigation.

THE UNIVERSITY,
GLASGOW.

LXVII.—*Influence of Non-electrolytes and Electrolytes on the Solubility of Sparingly Soluble Gases in Water. The Question of Hydrates in Solution.*

By JAMES CHARLES PHILIP.

MANY investigations have recently been made on the extent to which the solvent power of water for neutral gases is affected by the addition of various substances, both non-electrolytes and electrolytes (see, for example, Steiner, *Wied. Annalen*, 1894, **52**, 275; Gordon, *Zeitsch. physikal. Chem.*, 1895, **18**, 1; Jahn, *ibid.*, **18**, 8; Roth, *ibid.*, **24**, 114; Braun, *ibid.*, 1900, **33**, 721; Knopp, *ibid.*, 1904, **48**, 97; Hüfner, *ibid.*, 1907, **57**, 611). The gases studied have been chiefly hydrogen, nitrogen, and nitrous oxide, and the results show that the solubility of each of these gases is markedly less in a salt solution than it is in water. The relation between the diminution of solubility and the concentration of the salt is generally expressed by the empirical formula $(\alpha - \alpha')/M^{\frac{2}{3}} =$ a const., where α and α' are the absorption coefficients for the gas in pure water and salt solution respectively, and M is the number of gram-molecules of salt per unit volume of the solution. It has not been found possible to represent the influence of non-electrolytes on the solubility of gases in a similar manner; the difference $\alpha - \alpha'$ is sometimes very small in the case of non-electrolytes, and, generally speaking, their effect in lowering the solubility of gases is much less than that due to salts. Provided the solutions of the non-electrolytes are dilute, the relation $C_1/C_2 = 1$, where C_1 and C_2 are the molecular concentrations of the gas dissolved to saturation, firstly in pure water, and secondly in a non-electrolytic solution, has been deduced theoretically by Jahn, and verified experimentally in a number of cases. But this formula is not applicable to the absorption of gases by salt solutions, and hence the desire arises to find some common foundation on which the representation of the behaviour of electrolytes and non-electrolytes alike may be based.

It is here suggested that the influence of electrolytes and non-electrolytes on the solubility of gases may be adequately interpreted by reference to two factors. Firstly, it may be supposed that in the majority of cases, at least, the electrolyte or non-electrolyte is not responsible for any of the absorption, and accordingly the standard absorbing volume should be, not 1 c.c. or 1000 c.c. of the solution, but that volume of the solution which contains 1 gram or 1000 grams of the pure solvent. Secondly, hydration of the electrolyte or non-electrolyte may occur, and it may be supposed that the solvent which is thus attached is no longer free to absorb the gas. The latter suggestion has already been brought forward in a general way (see, for example, Baur, *Ahrens' Sammlung*, 1903, **8**, 466; Lowry, *Trans. Faraday Soc.*, July, 1905).

The importance of the first of these two considerations has lately been made evident by the work of Morse and Frazer on the osmotic pressure of aqueous solutions of sucrose and dextrose (*Amer. Chem. J.*, 1905, **34**, 1; 1906, **36**, 1, 39). These investigators have shown that the gas laws are applicable even to fairly concentrated solutions of these substances, provided one takes as the standard osmotic volume, not 1 litre of solution, but the volume of solution which contains 1000 grams of water. In other cases also the method of referring concentration, not to 1 litre of solution, but to 1000 grams of water, has yielded interesting results (see Cohen, *Zeitsch. physikal. Chem.*, 1897, **23**, 442; Caldwell, *Proc. Roy. Soc.*, 1906, *A*, **78**, 272).

The experimental material available for testing the two considerations just advanced is none too plentiful or too suitable. In the first place, it is obviously desirable that only those cases should be chosen in which the solubility of the dissolved gas is very small, and on this ground experiments with nitrous oxide will not be considered. In the second place, it must be said that the agreement between the results of different observers is not all that might be desired. In what follows, reference will be made chiefly to the work of Knopp (*loc. cit.*) and Steiner (*loc. cit.*).

Knopp has determined the solubility of hydrogen in chloral hydrate solutions, and finds that the absorption coefficient falls regularly as the concentration of the chloral hydrate increases. The absorption coefficient in pure water at 20° is 0·01883, that is, 1000 grams of water absorb practically 18·83 c.c. of hydrogen at 20°. At this temperature the absorption coefficient in a 7·69 per cent. solution of chloral hydrate is 0·01802, that is, 1 litre of this solution absorbs 18·02 c.c. of hydrogen. But a determination of the density shows that 1 litre of this solution contains only 952·4 grams of water, the absorbing substance, hence the values for the absorption coefficient in pure water and in the solution cannot properly be compared. If, however, that volume of solution were taken which contains 1000 grams of water, the volume of hydrogen absorbed would be $18{\cdot}02 \times \frac{1000}{952{\cdot}4} = 18{\cdot}92$ c.c., practically the same volume as is absorbed by 1000 grams of pure water at the same temperature. For other solutions of chloral hydrate up to 30 per cent. strength, corresponding to something above $2N$ concentration, a similar result is obtained, as is shown in the following table. The second column contains Knopp's data, the third column gives the figures, calculated as above, for the quantity of hydrogen absorbed by that volume of the solution which contains 1000 grams of water :

TABLE I.

Percentage of chloral hydrate.	Volume of hydrogen absorbed	
	by 1 litre of solution.	by 1000 grams of water.
4·91	18·39 c.c.	18·95 c.c.
7·69	18·02 ,,	18·92 ,,
14·56	17·12 ,,	18·78 ,,
18·77	16·53 ,,	18·69 ,,
29·5	15·42 ,,	19·07 ,.

So far as the table goes, the calculated values differ only slightly (mostly less than 1 per cent.) from the expected value 18·83, but if a similar calculation is made for the still more concentrated solutions employed by Knopp, the numbers obtained rise considerably higher.

In the foregoing calculations it has been tacitly assumed that the second main factor which is supposed to govern the diminution of solubility, namely, hydration, may here be left out of account. This procedure is justified by the work on the freezing points of aqueous solutions of chloral hydrate carried out by Jones and Getman, who have shown that chloral hydrate exerts no concentrating effect due to further combination with the solvent (see *Amer. Chem. J.*, 1904, 32, 319).

A non-electrolyte which Jones and Getman's work has shown to exist in solution in a hydrated form is sucrose, and it is therefore interesting to find that this substance is especially effective in lowering the solubility of hydrogen in water. The only data available are those recorded by Steiner (*loc. cit.*), and although his value for the absorption coefficient of hydrogen in water is lower than the values found by later observers, his results may be compared among themselves. For the absorption coefficient of hydrogen in water and in sucrose solutions at 15°, he found the values given in the second column of Table II.

TABLE II.

Percentage of sucrose.	Volume of hydrogen absorbed		Molecules of water to 1 molecule of sucrose.
	by 1 litre of solution.	by 1000 grams of water.	
0·00	18·83 c.c.	18·83 c.c.	—
16·67	15·61 ,,	17·5 ,,	6·7
30·08	12·84 ,,	16·3 ,,	5·9
47·65	8·92 ,,	14·0 ,,	5·4

The numbers in the third column have been obtained in the way described in connexion with chloral hydrate, and it will be observed that they diminish regularly; that is, the first of the two factors suggested is not alone sufficient to account for the influence of sucrose in lowering the solubility of hydrogen. If, as is suggested here, hydration is the other chief factor to be reckoned with, the defect of the numbers in the third column from 18·83 will be a measure of the extent of hydration. Thus, that volume of a 16·67 per cent. sucrose solution which contains 1000 grams of water will absorb 17·5 c.c. of hydrogen. If the water were all "free," it should absorb 18·83 c.c. of hydrogen, and hence the conclusion may be drawn that the fraction $\frac{18{\cdot}83 - 17{\cdot}5}{18{\cdot}83} = \frac{1{\cdot}33}{18{\cdot}83}$ of the water present is attached to the solute. Hence the average number of the water molecules which are attached to one molecule of sucrose is $\frac{1{\cdot}33 \times 83{\cdot}33 \times 342}{18{\cdot}83 \times 16{\cdot}67 \times 18} = 6{\cdot}7$. So for the more concentrated solutions the average hydrates are those with 5·9 and 5·4 molecules of water respectively, as recorded in the last column of Table II. The variation in these numbers with dilution is that required by the law of mass action, and it is noteworthy that the extent of hydration deduced in this way is very nearly that deduced by Jones and Getman from their freezing-point experiments. They found that the average number of water molecules associated in solution with one molecule of sucrose was in almost all cases between 5 and 8.

As Jones and Getman's results are valid for 0°, it is to be expected that the hydrates indicated by their work would be rather more complex than those existing at 15°.

The behaviour of electrolytes, as well as that of non-electrolytes, can be interpreted by reference to the two factors already suggested. In the case of electrolytes, the influence of the second factor, the hydration, predominates, and it is possible, as in the case of sucrose, to deduce the average molecular hydration of an electrolyte from the effect which it has in lowering the solubility of hydrogen. When Knopp's work on the solubility of hydrogen in potassium chloride solutions at 20° is examined in this way, the following values are obtained for the average molecular hydration of the salt:

TABLE III.

Percentage of potassium chloride.	Average molecular hydration.
1·09	9·8
2·12	11·1
4·07	10
6·37	10
7·38	10
13·61	7·6

From Steiner's results an average molecular hydration of 9·4 is similarly deduced for a 7·48 per cent. solution of potassium chloride. The values here calculated for the average molecular hydration of potassium chloride are considerably lower than those ($26H_2O$ to $15H_2O$ for solutions of concentration $N/10$ to $N/2$) deduced by Biltz in his study of the freezing-point depression (*Zeitsch. physikal. Chem.*, 1902, **40**, 220), but are in close agreement with the figure ($11H_2O$ for $N/1$ solution) recently recorded by Caldwell (*loc. cit.*).

The solubility of hydrogen in sodium chloride solutions has been determined by Braun (*loc. cit.*), and although the experimental data here available are not quite so satisfactory, it may be shown as before that the average molecular hydration increases from 9·2 for a 6 per cent. solution to 15·4 for a 1·52 per cent. solution. According to Biltz (*loc. cit.*), the molecular hydration increases from 19 for an $N/2$ solution to 25 for an $N/10$ solution, whilst Caldwell finds that in a solution containing 1 gram-molecule of sodium chloride per 1000 grams of water the average molecular hydration is 13. When Braun's experiments on the influence of sodium chloride on the absorption coefficient of nitrogen are taken as the basis of calculation, higher values (18·3 in a 6·4 per cent. solution) are obtained for the average molecular hydration.

From Steiner's work it may similarly be shown that in a normal solution of calcium chloride each molecule of solute is associated with, on the average, about 21 molecules of water. Studying the influence of this salt on the rate of inversion of sucrose, Caldwell arrives at the figure 22 as representing the molecular hydration.

When Knopp's accurate work on the absorption of hydrogen by solutions of ammonium, potassium, and sodium nitrates is studied from the point of view suggested in this paper, the interesting conclusion is reached that in *N*/1 solution the molecular hydration is approximately 2 for ammonium nitrate, 6 for potassium nitrate, and 11 for sodium nitrate.

On the lines already laid down, the influence of electrolytes on the solubility, not only of a neutral gas, but also of a neutral solid, such as phenylthiocarbamide, can be adequately interpreted. From Biltz's determinations of the solubility of phenylthiocarbamide at 20° in solutions of sodium, potassium, and barium chlorides (*Zeitsch. physikal. Chem.*, 1903, **43**, 41) the average molecular hydration of these salts may be calculated exactly in the manner already described. For the calculation of the molecular hydration the densities of the solutions at 20° are required, and as these are not recorded in Biltz's paper they have been determined. The values found are given in the following table:

TABLE IV.

	Potassium chloride.		Sodium chloride.		Barium chloride.	
Concentration.	Density.	Average molecular hydration.	Density.	Average molecular hydration.	Density.	Average molecular hydration.
N/1	1·0450	11·9	1·0385	14·5	1·0885	26·2
N/2	1·0219	12·3	1·0163	14·8	1·0437	25·6
N/4	1·0102	17·4	1·0085	16·3	1·0210	29·8

The values found in this way for the molecular hydration of potassium and sodium chlorides agree fairly well with those already deduced in this paper or calculated by other methods. For barium chloride Caldwell estimates the average molecular hydration in a normal solution at 19, a value somewhat lower than those deduced from Biltz's experiments and recorded in the foregoing table.

It appears possible, therefore, to interpret generally the behaviour of non-electrolytes and electrolytes alike by reference to the two factors suggested in the beginning of this paper. It is, further, noteworthy that the values found for the molecular hydration of dissolved salts by the various methods should agree as closely as they do, especially when it is borne in mind that the phenomena on which these values are based differ so widely as the absorption of gases, the depression of the freezing point, and the inversion of sucrose.

Royal College of Science,
South Kensington, S.W.

LXVIII.—*Organic Derivatives of Silicon. Part III.* dl-*Benzylmethylethylpropylsilicane and Experiments on the Resolution of its Sulphonic Derivative.*

By Frederic Stanley Kipping.

The *dl*-sulphonic acid obtained by heating phenylbenzylethylpropylsilicane with sulphuric acid, and the resolution of which into its optically active components has recently been recorded (Part II, this vol., p. 209), is a derivative of benzylethylpropylsilicol, the phenyl group of the silicohydrocarbon being eliminated as benzene previous to or during sulphonation (*loc. cit.*, p. 223). This being the case, it seemed expedient to try to obtain benzylethylpropylsilicol by a more direct method, and to avoid the trouble of first introducing a phenyl radicle into, and then displacing it from, the molecule of the silicon compound. With this end in view, ethylsilicon trichloride was treated with magnesium benzyl chloride; the interaction proceeded normally, and the yield of *benzylethylsilicon dichloride*, $BzEtSiCl_2$, was satisfactory, although the formation of dibenzyl and of other by-products could not be avoided.

Benzylethylpropylsilicyl chloride, BzEtPrSiCl, was then prepared by the interaction of the benzylethyl derivative and magnesium propyl bromide, but in this case the yield was poor, owing to secondary reactions, and also because when molecular quantities are employed, a considerable proportion of the benzylethyl compound remains unchanged.

A few experiments were made with this *dl*-chloride in order to test its suitability for the preparation of an optically active silicon compound. It was caused to react with *p*-toluidine, but the resulting amine, $BzEtPrSi{\cdot}NH{\cdot}C_6H_4Me$, was an oil, and so unstable towards water that it seemed useless to prepare corresponding derivatives of optically active bases in order to try to resolve them by fractional crystallisation. The chloride was also treated with silver *d*-bromocamphorsulphonate, but apparently the silicyl ester was not formed, the results of these experiments confirming on the whole those previously described in the case of phenylethylpropylsilicyl chloride and silver camphorsulphonate (*loc. cit.*, p. 220). The interaction of benzylethylpropylsilicyl chloride and ethyl sodioacetoacetate was also investigated in the hope of ultimately obtaining a carboxylic acid, $BzEtPrSi\cdot CH_2\cdot CO_2H$, which might be resolved, but the results were very unsatisfactory, and a definite product was not isolated.

The decomposition of the chloride with water led to the formation of a mixture of *benzylethylpropylsilicol*, $BzEtPrSi\cdot OH$, and the corresponding oxide, $(BzEtPrSi)_2O$, and although various attempts were made to diminish the proportion of the latter, they met with no success, nor have the conditions favourable to the conversion of the silicol into the oxide been determined, although certain observations seem to show that the change takes place spontaneously even at the ordinary temperature.

This instability of the tertiary silicol is a noteworthy fact, and seems to be a general property of such compounds, or, at any rate, of those which contain an aromatic radicle.

Benzylethylpropylsilicol is sulphonated very rapidly when it is heated with ordinary sulphuric acid at 90—100°; the product is not homogeneous and seems to consist of two acids. One of these is easily isolated in the form of its ammonium salt, and is identical with the acid obtained by the sulphonation of phenylbenzylethylpropylsilicane under the conditions previously described (this vol., p. 224). This acid, for the reasons already given, may be regarded as a derivative of benzylethylpropylsilicyl oxide; its preparation by the method now described (p. 727) is infinitely preferable to that involving the use of phenylbenzylethylpropylsilicane. The second product of the sulphonation of the silicol has not yet been examined; obviously it may be the internally compensated isomeride of the compound which has been resolved.

As the results of the investigation of the sulphonic acid, obtained from phenylbenzylethylpropylsilicane and from benzylethylpropylsilicol, gradually led to the conclusion that it was probably derived from the oxide, and as many attempts to resolve it were unsuccessful, it seemed possible at one time that it might be the internally compensated compound; consequently this acid lost its interest to a great extent, and its further study was temporarily abandoned.

A more promising line of investigation seemed to offer itself in the synthesis of a silicohydrocarbon such as benzylmethylethylpropylsilicane, BzMeEtPrSi, which would contain the benzyl group necessary for the subsequent formation of a sulphonic acid, but which, owing to the absence of hydroxyl, could not yield a condensation product comparable to that formed from the silicol.

dl-*Benzylmethylethylpropylsilicane* was therefore prepared by the action of magnesium methyl iodide on benzylethylpropylsilicyl chloride and was isolated without difficulty; as it was found to sulphonate comparatively easily, the isolation of the sulphonic derivative and its resolution into optically active components seemed to be almost accomplished facts.

But in the case of silicon compounds, in spite of their analogy with those of carbon, anticipations are not always realised; the product of sulphonation proved to be a mixture, which for a long time very successfully defied all the author's attempts to isolate from it a definite compound. Ultimately it yielded two acids which were obtained in a pure condition in the form of their *l*-menthylamine salts. The one of these seemed to be present in relatively very small quantities; its analysis showed that it was not derived directly from the silicohydrocarbon, but from benzylethylpropylsilicol; it is concluded, therefore, that the methyl group of the benzylmethylethylpropylsilicane is eliminated by the sulphuric acid in a manner similar to that in which the phenyl group of phenylbenzylethylpropylsilicane is hydrolysed (this vol., p. 223).

The other *l*-methylamine salt was a well-defined compound derived from *benzylmethylethylpropylsilicanesulphonic acid*,

$$MeEtPrSi{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H,$$

but the quantity obtained after weeks of fractional crystallisation, was so small that the prospect of preparing sufficient material for resolution experiments was by no means inviting. The use of chlorosulphonic acid, in place of sulphuric acid, as sulphonating agent, made an extraordinary difference; at 0°, the silicohydrocarbon was converted into a product, from which the pure *l*-menthylamine salt could be easily obtained in the course of a few hours and in very satisfactory quantities.

This *l*-menthylamine salt is a very well characterised substance, and it has played an important part in this investigation; it crystallises so well and so readily, perhaps more so than any other salt which has been prepared, that it has been repeatedly used in the isolation and identification of the acid. Its molecular weight in methyl-alcoholic solution was found to be normal, but in other solvents the results indicated a high degree of association.

Fractional crystallisation of this *l*-menthylamine salt left it unchanged, and although up to the present at least seven different salts of benzylmethylethylpropylsilicanesulphonic acid with optically active bases have been very carefully examined and a number of others more superficially studied, not the slightest indication of a resolution of the acid has been observed.

This interesting but troublesome behaviour recalls that of secondary butylbenzenesulphonic acid, $CHMeEt\cdot C_6H_4\cdot SO_3H$, which was recently examined by Klages (*Ber.*, 1906, **39**, 2131), who attempted in vain to accomplish the resolution of several of its alkaloidal salts.

That benzylmethylethylpropylsilicanesulphonic acid and this benzenesulphonic acid are not easily resolved can hardly be attributed in any way to the presence of the sulphonic group, inasmuch as the optically active sulphonic acids of camphor are generally so efficient in resolving *dl*-bases; nor apparently does association play any part, the molecular weight of the *l*-menthylamine salt of the silicanesulphonic acid being normal in methyl-alcoholic solution.

It seems more likely that, in consequence of the similarity of the homologous alkyl groups, the asymmetry of the silicon molecule is not sufficiently pronounced; in the case of some carbon compounds, the constitution of which, in this respect, is comparable to that of the acid in question, resolution is sometimes accomplished, only after prolonged fractional crystallisation, involving the use of large quantities of material, as found by Schültz and Marckwald for example, who crystallised about 1190 grams of the brucine salt of α-methylbutyric acid twenty times before obtaining an optically pure preparation.

Nevertheless, further attempts are being made with this silicon derivative, and other acids of a like structure, but in which the silicon is combined with more dissimilar alkyl groups, are also being studied.

Benzylethylsilicon Dichloride, $EtBzSiCl_2$.

The interaction of ethylsilicon trichloride and magnesium benzyl chloride in ethereal solution results in the formation of benzylethylsilicon dichloride, dibenzylethylsilicyl chloride, and apparently other compounds; the crude product also contains moderate quantities of dibenzyl. To avoid the formation of this hydrocarbon as far as possible, the preparation of the magnesium benzyl chloride is carried out at 0°, after the reaction has once started, using an efficient stirrer; to allow for its formation, 17 grams of magnesium are employed for 100 grams of the ethylsilicon trichloride, instead of the theoretical quantity.

The green ethereal solution thus obtained is added drop by drop to the silicon compound, previously mixed with a little ether and cooled in ice; the separation of magnesium chloride commences immediately and there is a development of heat, so that vigorous stirring is advisable during the whole operation. When the magnesium compound has been added, the mixture is left at the ordinary temperature for twelve to twenty-four hours, during which time a further separation of magnesium chloride occurs. The ethereal solution is then filtered and the residue repeatedly washed with ether in one of the forms of apparatus already described (this vol., p. 216).

The filtrate and washings give on evaporation a dark yellow or brown, fuming liquid which contains, in addition to the compounds named above, ether, ethylsilicon trichloride, and benzyl chloride. This mixture is first distilled from an ordinary Würtz flask until the thermometer indicates about 130° and the pressure is then reduced to 100 mm.; most of the liquid now passes over between 160° and 180° and is collected separately. Above this temperature the thermometer begins to rise more rapidly and the fraction collected from 180° to 200° contains but little of the desired product; the residue, which consists of dibenzyl, dibenzylethylsilicyl chloride, and other compounds has been examined in conjunction with Mr. R. Robinson, and the results will be communicated later.

The benzylethylsilicon dichloride is isolated from the fractions 160—180° and 180—200° (100 mm.) by systematic fractional distillation under 100 mm. pressure, using a long necked flask fitted with a rod and disc column (this vol., p. 215); this operation is rendered rather troublesome, apparently by the presence of dibenzyl, which seems to pass over at temperatures far below its real boiling point; but finally the material is resolved into a very large fraction boiling at 168—170°, and very small ones of lower and of higher boiling point. A little ethylsilicon trichloride may be recovered from the original distillate collected up to 130° under atmospheric pressure (see above).

The liquid boiling at 168—170° (100 mm.), the yield of which is 60—80 per cent. of the theoretical, is sufficiently pure to be used directly for the preparation of other derivatives; it contains, however, small quantities of impurity—probably dibenzyl—and on analysis is found to contain only about 31 per cent. of chlorine.

The pure compound is obtained after two or three more distillations, the last portions being rejected each time; a specimen thus prepared was found to contain 31·9 per cent. of chlorine, the halogen being determined volumetrically (compare this vol., p. 217); a different sample was analysed gravimetrically:

0·5203 gave 0·6670 AgCl. Cl = 31·7.

$C_9H_{12}Cl_2Si$ requires Cl = 32·3 per cent.

Benzylethylsilicon dichloride is a colourless, mobile, fuming liquid, boiling at 169° (thermometer thread entirely in vapour; pressure 100 mm.); it soon turns a faint pink and when kept for some time it becomes yellow unless highly purified; it is immediately decomposed by water, giving *benzylethylsilicone*, a compound which has been investigated in conjunction with Mr. R. Robinson, and an account of which is therefore postponed.

Benzylethylpropylsilicyl Chloride, SiBzEtPrCl.

When an ethereal solution of magnesium propyl bromide (1 mol.) is added to benzylethylsilicon dichloride (1 mol.), there is only a very slight development of heat, and the solutions may be mixed fairly rapidly, cooling merely with water; at first no separation of magnesium salt occurs, but on keeping at the ordinary temperature during about twenty-four hours a considerable deposit is formed. In order to complete the interaction the mixture is first boiled for some time, using a reflux condenser; the ether is then distilled off and the residue heated on the water-bath during three to four hours.

The pasty mass of oil and magnesium salt is now transferred to one of the forms of apparatus already described, with the aid of the ether, which has been distilled off, and the product is separated by filtering and repeatedly washing with ether in the usual way; on evaporating the ethereal solution there is almost invariably a further separation of magnesium salt, which may necessitate a repetition of these processes. The filtrate and extracts then give on evaporation an almost colourless liquid, which is first distilled from an ordinary Würtz flask under a pressure of 100 mm.; very little passes over below about 185°, but a very large proportion distils between 180° and 215°, and is collected separately; above this temperature the thermometer continues to rise rather rapidly to 360° or higher, and there is often a considerable quantity of magnesium salt left in the flask, even when the original liquid was quite clear.

The portion of the crude product which boils above 215° (100 mm.) is a viscid, fuming oil, which contains little, if any, benzylethylpropylsilicyl chloride; the last-named compound is obtained by systematically fractionating the portion boiling from 180—215°, using a long-necked flask fitted with a rod and disc column. Owing apparently to the presence of a moderate quantity of unchanged benzylethylsilicon dichloride, the boiling point at first rises rather slowly from about 175° to about 190° (100 mm.); the greater part then distils between 190° and 200°, but even after repeated fractionation the boiling point does not become very definite, so that it is difficult to ascertain what is the true boiling point of this propyl derivative. At first it was thought to be about 190°, but various specimens collected at this temperature were found to contain 16·8 to 17·8 per cent. of chlorine instead of the theoretical quantity, namely, 15·7 per cent. In later experiments samples boiling at 194—196° and at 196—198° were collected and analysed with the following results:

Fraction 194—196°/100 mm. 0·5988 gave 0·3826 AgCl; Cl = 15·7.
Fraction 196—198°/100 mm. 0·6606 gave 0·4071 AgCl; Cl = 15·2.
$C_{12}H_{19}ClSi$ requires Cl = 15·7 per cent.

These results seemed to show that the boiling point was about 195°, and that the fractions collected above this temperature contained a little benzylethyldipropylsilicane. In the hope that a substance of more constant boiling point might be obtained by fractionating under different conditions, various specimens were repeatedly distilled under a pressure of 50 mm., but the results were no better than before; the fraction collected from 172—176° (50 mm.) certainly gave satisfactory results on analysis:

0·2947 gave 0·1885 AgCl. Cl = 15·8 per cent.,

but a product of really constant boiling point could not be obtained in any large quantity.

Benzylethylpropylsilicyl chloride is a colourless, fuming, mobile liquid, which generally becomes slightly pink after a short time, apparently owing to the presence of traces of iodine;* it is immediately decomposed by water, giving a mixture of the corresponding alcohol and oxide (p. 726).

If air be admitted, after distilling under reduced pressure, while the apparatus is still hot and full of vapour of benzylethylpropylsilicyl chloride, spontaneous ignition often occurs with separation of carbon.

The liquid boiling above 215° (100 mm.) collected from various preparations of this propyl derivative was fractionated under a pressure of 50 mm.; the thermometer rose rapidly from 215° to about 290°, fairly slowly from 290° to 320°, and then more quickly up to 380° or higher. The liquid passing over, from about 290°, is a viscid, yellow oil, which shows a green fluorescence and fumes in the air; the portion boiling from 360° upwards fumes very little. These liquids doubtless contain some very interesting compounds, possibly some having a closed chain structure, but their investigation has not yet been attempted.

It is difficult to state exactly the yield of pure propyl derivative in the above method of preparation, but the quantity of product sufficiently pure for use in further experiments may be taken as from 50—60 per cent. of the theoretical.

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* Several specimens of propyl bromide were found to contain a little combined iodine.

Interaction of Benzylethylpropylsilicyl Chloride and Silver d-*Bromocamphorsulphonate.*

Although the attempts to obtain the *d*-camphorsulphonate of phenylethylpropylsilicol were quite fruitless (this vol., p. 220), the interaction of the compounds named above was investigated, more in the expectation of confirming previous results than in the hope of forming a stable ester in accordance with the following equation:

$$\mathrm{SiBzEtPrCl} + \mathrm{C_{10}H_{14}BrO{\cdot}SO_3Ag} = \mathrm{SiBzEtPr{\cdot}SO_3{\cdot}C_{10}H_{14}BrO} + \mathrm{AgCl}.$$

Silver bromocamphorsulphonate, finely powdered and dried at 100°, was gradually added, finally in slight excess, to an ethereal solution of the silicon compound; an immediate separation of silver chloride occurred at first, but the last small quantity added seemed to be unchanged. The solution, which was only slightly turbid, was immediately decanted, and the residue rapidly washed two or three times with dry ether; this residue, on examination, was found to contain a small quantity of silver bromocamphorsulphonate, but otherwise consisted only of silver chloride.

The ethereal solution and washings, having been evaporated out of contact with moisture, separated into two layers, and were then mixed with dry light petroleum; this dissolved the upper layer, and the solution was decanted from the lower one, which was found to consist of practically pure bromocamphorsulphonic acid (as it dissolved in water giving a clear solution, and solidified on exposure to moist air giving the hydrated crystals of the acid).

The petroleum solution gave on evaporation an oil which distilled without decomposing when heated in small quantities under atmospheric pressure; as this product could not possibly be the ester, it was washed with a little water (which only extracted traces of the bromo-acid), dried, and distilled under a pressure of about 70 mm.; it boiled from about 220° to above 350°, and yielded nothing more definite than a main fraction collected from 265° to 290° which possibly consisted of impure benzylethylpropylsilicyl oxide, $\mathrm{(SiBzEtPr)_2O}$ (p. 727).

As in the above experiment water was rigidly excluded until it was found that the bromocamphorsulphonic acid had not combined with the silicon compound, it seems clear that the interaction expressed in the above equation does not take place; what really occurs is by no means obvious, but possibly hydrogen chloride is eliminated from the silicon compound, which then undergoes polymerisation. In one respect the reaction seems to differ from that occurring between phenylethylpropylsilicyl chloride and silver camphorsulphonate, namely, that in the latter case a considerable proportion of the chloride is converted into the corresponding silicol, whereas with the benzyl derivative very little, if any, such product appears to result.

Benzylethylpropylsilicyl-p-*toluidide*, $EtPrBzSi\cdot NH\cdot C_6H_4Me$.

Experiments with phenylethylpropylsilicyl chloride having shown that compounds of the type $SiR_3\cdot NHR$ are decomposed by water (this vol., p. 219), there did not seem to be much prospect of obtaining a very stable compound by the interaction of benzylethylpropylsilicyl chloride and *p*-toluidine. However, as the introduction of a benzyl in place of a phenyl group exercises a considerable influence on some of the properties of the silicon compound, it was not impossible that this might also be the case as regards the stability of the union between nitrogen and silicon, and if so, suitable products might be utilised for the resolution of silicon derivatives.

Benzylethylpropylsilicyl chloride was therefore dissolved in dry ether, and a solution of *p*-toluidine (2 mols.) in the same solvent gradually added, moisture being excluded; an immediate separation of *p*-toluidine hydrochloride occurred, and as soon as the reaction was completed, the solution was rapidly filtered and the residue washed with dry ether. The filtrate, on evaporation, gave a yellow oil, which was mixed with dry light petroleum; this caused the precipitation of a further quantity of *p*-toluidine hydrochloride, free from any crystalline silicon compound.

As the oil which remained after distilling off the petroleum did not crystallise, it was fractionated under a pressure of about 70 mm., and the main product, which passed over at about 260—270°, collected separately and redistilled. This substance was a yellow, rather viscous liquid boiling from 260—265° (70 mm.); it contained nitrogen, was immediately decomposed by concentrated sulphuric acid, giving *p*-toluidine sulphate and an oil, and on exposure to the air it slowly deposited crystals of *p*-toluidine owing to its decomposition by atmospheric moisture. As the compound was found to be unstable towards water it was not further examined.

Interaction of Benzylethylpropylsilicyl Chloride and Ethyl Sodioacetoacetate.

Very few experiments have yet been made with the object of preparing a carboxylic acid derivative of silicon which might be used for the resolution of suitable compounds; of such, one only will be described here, namely, an attempt to realise the following equation:

$$SiBzEtPrCl + CH_3\cdot CO\cdot CHNa\cdot CO_2Et = SiBzEtPr\cdot CHAc\cdot CO_2Et + NaCl$$

A solution of benzylethylpropylsilicyl chloride in dry ether was gradually added to the theoretical quantity of ethyl sodioacetoacetate (Kahlbaum), and as no appreciable reaction occurred, the ether was soon distilled off and the residue heated on the water-bath during about two hours, moisture being excluded.

At the end of this time (a portion of the product having been tested and found to be free from benzylethylpropylsilicyl chloride), first water and then dilute sulphuric acid were added, and the oily liquid was then extracted with ether; the solution gave, on evaporation, a yellow oil, which was fractionated under a pressure of 35 mm., and thus found to be far from homogeneous. Commencing to boil at about 100°, about 50 per cent. passed over from 110° to 170°; the thermometer then rose more rapidly, and almost continually to above 300°, at which temperature there still remained a little oil in the distillation flask. The different fractions collected were heated during several hours with alcoholic sodium hydroxide and then examined, but they seemed to be unchanged; at any rate, they did not afford any acid insoluble or sparingly soluble in water.

It seems, therefore, that the interaction expressed by the above equation does not occur, and as large quantities of the silicon compound would be required to investigate it thoroughly, its further study has been postponed.

Benzylethylpropylsilicol, SiBzEtPr·OH.

The decomposition of benzylethylpropylsilicyl chloride with water is attended by only a slight development of heat; the product does not consist of the pure silicol, SiBzEtPr·OH, as might have been expected, but of a mixture of the latter with a considerable quantity of a substance of much higher boiling point, doubtless the ether * or oxide, $(SiBzEtPr)_2O$.

As the production of this oxide might be due to the action of the hydrochloric acid formed in the process, in some experiments the silicon compound was poured into an ice-cold saturated solution of sodium acetate instead of into water, but apparently without influencing the course of the reaction to an appreciable extent; it was also decomposed with sodium carbonate solution in various ways, but the relative proportion of oxide did not seem to change.

The colourless oil resulting from the interaction, isolated by extracting with ether and distilled under a pressure of 25 mm., begins to boil at about 150°, and gives a large fraction between 150° and 165°; the thermometer then rises rapidly to about 250°, and another large fraction passes over from 250° to 260°, but even above this temperature small quantities of a very viscid liquid sometimes distil over slowly, the thermometer indicating more than 300°.

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* The term "ether" seems so inapplicable in the case of these silicon compounds of high boiling point that "oxide" is generally employed instead.

As the formation of water is not observed during distillation, it may be inferred that the oxide is present in the original product; this conclusion is borne out by the following analysis of a specimen of the undistilled oil which had been kept over sulphuric acid during some days:

0·5075 gave 0·1510 SiO_2. Si = 14·0.

SiBzEtPr·OH requires Si = 13·6; $(SiBzEtPr)_2O$ requires Si = 14·2 per cent.

The fraction collected between 150° and 165° yields on redistillation a liquid boiling at about 155° (25 mm.), but slight changes in pressure and vigorous "bumping" by the liquid make it rather difficult to observe the boiling point very accurately; that this product consists of the silicol is shown by the following analysis:

0·2154 gave 0·5474 CO_2 and 0·1858 H_2O. O = 69·3; H = 9·6.

SiBzEtPr·OH requires C = 69·2; H = 9·6 per cent.

Benzylethylpropylsilicol is a colourless, fairly mobile liquid specifically lighter than water (both at about 16°), in which it is practically insoluble; it has when warm a rather strong and pleasant aromatic odour. Hitherto its properties have been only superficially examined except as regards its behaviour towards sulphuric acid, but it may be stated that a specimen of about 12 grams, which was left in an open test-tube, became cloudy, and in the course of some days deposited drops of water; on redistilling, only about 5 grams of alcohol were obtained, the rest having changed into the oxide.

The fraction of the crude product collected from 250—260° (see above), which doubtless consists of the oxide, is a viscid, colourless liquid; one specimen was analysed with the following result:

0·4254 gave 0·1350 SiO_2. Si = 14·9 per cent.

But this product, like many others, awaits further investigation.

The small quantity of very viscous liquid passing over in the neighbourhood of 300° (see above) is possibly benzylethylsilicone, BzEtSiO, resulting from the decomposition of a little benzylethylsilicon dichloride which may have been present in some of the samples of propyl derivative used for the preparation of the silicol.

Sulphonation of Benzylethylpropylsilicol with Sulphuric Acid.

It has already been stated that phenylbenzylethylpropylsilicane is decomposed by warm concentrated sulphuric acid, giving benzene and benzylethylpropylsilicol; also that the latter, when further heated with the acid in presence of the benzene, gradually undergoes sulphonation, yielding a mixture of acids from which the pure sulphonic derivative of benzylethylpropylsilicyl oxide can be isolated, but only with very considerable difficulty, in the form of its ammonium salt (this vol., p. 224).

The sulphonic acid just mentioned is far more conveniently prepared by sulphonating pure benzylethylpropylsilicol. For this purpose, the silicol, in quantities of about 5 grams at a time, is placed in a small flask with 1½—2 volumes of ordinary concentrated sulphuric acid, and the flask is then rapidly heated in a bath of fusible metal, shaking vigorously from time to time; the external heating, and the heat developed by the interaction, jointly bring about a rapid rise of temperature, and a thermometer immersed in the mixture rises very quickly. As soon as the mixture has reached 100° the flask is removed from the bath and cooled by immersion in water; the whole operation is at an end in less than a minute, and a portion of the product should then give a perfectly clear solution if poured into a large volume of water.

Sulphonation having been successfully carried out, the liquid, which separates into two layers if only about 1½ volumes of acid have been used, is poured into water; here again a separation occurs, unless the volume of water is considerable (which is unnecessary) and most of the sulphonic acid rises to the surface as a viscid, pale yellow oil; the addition of ammonia in slight excess gives, however, a clear homogeneous solution.

In order to isolate the ammonium salt, the solution is evaporated to a syrup, the ammonium sulphate precipitated with alcohol, and removed completely by again treating the filtered and evaporated solution with methyl alcohol; the viscous syrup ultimately obtained (compare this vol., p. 225) is carefully dried, dissolved in a very little hot methyl alcohol and the solution treated with ethyl acetate; when then allowed to cool over sulphuric acid it gives a thick, crystalline deposit of practically pure ammonium salt, and further quantities of the same substance are obtained from the filtrate. The yield of the pure salt of the sulphonic derivative is about equal to that of the silicol employed; the final mother liquors contain a pale yellow oil which seems to be the ammonium salt of a silicon sulphonic derivative, but which is readily soluble in ethyl acetate.

The ammonium salt thus prepared from benzylethylpropylsilicol crystallises far more readily than that obtained indirectly from phenylbenzylethylpropylsilicane, the latter being mixed with impurities which are not easily removed even after several recrystallisations; that the compounds from the two sources, however, are identical was proved by directly comparing the *l*-menthylamine and *d*-bornylamine salts produced from them by simple precipitation; melting point observations were also made with the salts from the two sources, both separately and with mixtures of corresponding compounds, and the results left no doubt as to their identity.

The *l*-menthylamine salt, obtained from the crude mixture of ammonium salts, isolated from the product of the sulphonation of phenylbenzylethylpropylsilicane, is so impure that it is very difficult, if not impossible, to remove the impurities by fractional crystallisation, and the ammonium salt must first be crystallised in the manner previously described. In the case of the sulphonation product of benzylethylpropylsilicol this is not so, and perhaps the quickest, although not the best way of isolating the sulphonic acid is to precipitate the *l*-menthylamine salt directly from the neutral solution of the ammonium salt without first removing the accompanying ammonium sulphate and the other ammonium salt contained in the solution; the precipitate is generally oily at first, but soon solidifies, and can be purified by crystallising two or three times from aqueous alcohol and several times from moist ethyl acetate. About 7 grams of pure hydrated *l*-menthylamine salt were thus obtained from 4—5 grams of benzylethylpropylsilicol; the rest of the menthylamine salt was more soluble and remained as a buttery mass on allowing the mother liquors to evaporate spontaneously.

Benzylmethylethylpropylsilicane, SiBzMeEtPr.

Benzylethylpropylsilicyl chloride does not react readily with an ethereal solution of magnesium methyl iodide; no appreciable rise of temperature occurs on mixing the two liquids rapidly, and there is no separation of magnesium salt; even when the ether is distilled off and the mixture left for some hours on the water-bath only a very slight precipitate is formed, but on heating in an air- or metal-bath at about 110—120°, the interaction seems to be complete at the end of about two hours.

The product, which consists of a viscid oil, covering a pasty mass of the magnesium salts, is poured into water, the solution extracted with ether, and the extract washed with sodium hydroxide solution (if necessary to remove iodine) and then with dilute sulphuric acid. The colourless oil obtained from the dried ethereal solution is now fractionated, either from an ordinary distilling flask under atmospheric pressure, or better from a long-necked flask fitted with a rod and disc column under reduced pressure (100 mm.); in the latter case, the liquid begins to boil at about 175° and most passes over between 178° and 190°, but there is generally left a moderate quantity of a viscid oil which continues to distil up to and above 300°.

The principal fraction is now treated with sodium, with which it is heated from time to time until all, if any, action ceases; it is then distilled in contact with the metal under atmospheric pressure and the portion passing over from 248—254° (755 mm.) collected separately.

Even when benzylethylpropylsilicyl chloride which is free from impurity (judging from chlorine determinations) is employed for the preparation of this silicohydrocarbon, the yield of the fraction 248—254° is unsatisfactory, namely, about 60 per cent. of the theoretical, and the product does not boil at a constant temperature even after several distillations; this may be due, possibly, to the displacement, to a small extent, of ethyl or propyl by methyl groups; whether this be so or not is merely a matter of conjecture, but there is little doubt that in most of these reactions between alkyl silicon chlorides and magnesium alkylhalogen compounds, changes occur other than the mere displacement of halogen by a hydrocarbon radicle.

Various preparations of this silicohydrocarbon have been analysed and the results agreed well with those required by theory:

I. 0·1381 gave 0·3817 CO_2 and 0·1401 H_2O. C = 75·4; H = 11·3.
II. 0·2126 „ 0·5862 CO_2 „ 0·2075 H_2O. C = 75·2; H = 10·8.
III. 0·2600 „ 0·7305 CO_2 „ 0·2546 H_2O. C = 75·5; H = 10·7.
„ 0·3028 „ 0·0748 SiO_2; Si = 13·1 per cent.

SiBzMeEtPr ($C_{13}H_{22}Si$) requires C = 75·6; H = 10·7; Si = 13·8 per cent.

Sample I boiled at 173—174° (100 mm.); II at 244—247° (750 mm.); III at 247—249° (760 mm.).

It may be pointed out, however, that the immediate homologues of this compound do not differ from it very much in percentage composition, benzyldimethylpropylsilicane, for example, containing C = 74·0 and H = 10·1 per cent., so that their presence in small quantities would not be indicated by the analytical results; more satisfactory evidence that the silicohydrocarbon really has the formula assigned to it is provided by a study of its product of sulphonation (p. 739).

Benzylmethylethylpropylsilicane is a colourless, mobile, highly refractive liquid having a rather pleasant aromatic odour; so far as has been ascertained its boiling point seems to be 250° (760 mm.) and about 177° under a pressure of 100 mm. The former compares satisfactorily with that of phenylmethylethylpropylsilicane (this vol., p. 221), which was found to be 228—230° (760 mm.). The silicohydrocarbon is specifically lighter than water, in which, of course, it is practically insoluble; it is miscible with all the ordinary organic solvents. Several attempts have been made, on a small scale, to obtain a nitro-derivative of this compound by the usual methods, but hitherto they have been unsuccessful; in other directions not even preliminary experiments have yet been made, and the whole behaviour of the compound, except towards sulphonating reagents, awaits further investigation.

Sulphonation of Benzylmethylethylpropylsilicane.

When benzylmethylethylpropylsilicane is shaken with ordinary concentrated sulphuric acid (about 2 vols.), the latter generally turns yellow, but the silicohydrocarbon does not dissolve to an appreciable extent, and remains practically unchanged even after the lapse of twenty-four hours; on warming at 60—70°, shaking from time to time, there is also very little action, but at 80—85° a slight evolution of sulphur dioxide sets in and in the course of about an hour sulphonation is complete, the product being completely soluble in water.

Contrary to what might have been expected, the reaction which occurs under the conditions just stated seems to be a highly complex one, nd experiments carried out, it is true only on a small scale, indicate the formation of a mixture of sulphonic acids from which it is difficult to isolate a silicon derivative.

Tho results are also highly unsatisfactory when sulphonation is carried out as rapidly as possible, as described below (a method which was found to work well in sulphonating benzylethylpropylsilicol, p. 728), the product being a mixture which yields pure crystalline compounds only after an exceedingly troublesome and prolonged course of fractional crystallisation applied to its menthylamine salts. For this reason, the experiments are described as briefly as possible; some account of them, however, is desirable, as they led to the preparation of a sulphonic acid which has not yet been obtained in other ways.

Benzylmethylpropylsilicane, in quantities of about 4 grams at a time, is treated with ordinary concentrated sulphuric acid (6—7 grams) in a small flask, which is then rapidly heated in a metal-bath; very little change occurs until a thermometer, placed in the flask, indicates about 130°, when a slight effervescence sets in owing to the escape of sulphur dioxide; if now, the contents of the flask are vigorously shaken, the mobile silicohydrocarbon suddenly becomes converted into a very viscid liquid, which, although it does not dissolve in the acid, is readily and completely soluble in water. The whole operation is finished in less than four minutes, and should the evolution of sulphur dioxide become more rapid when the flask is first shaken (at 130°) the temperature is immediately lowered by cooling in water.

The clear, yellow, aqueous solution of the product, which often shows an intense green fluorescence, is neutralised with ammonia, and the ammonium sulphate separated with the aid of methyl alcohol; the alcoholic solution is then evaporated, the yellow, buttery residue dried at 100°, and again dissolved in anhydrous methyl alcohol. From the concentrated solution ethyl acetate precipitates a small quantity of a crystalline powder, which appears to be a mixture of at least two ammonium salts and which seems to be produced in larger quantities the longer the period of sulphonation is extended; as this precipitate gave only traces of silica on ignition with sulphuric acid, it was not examined further.

The main products, which remain in the alcoholic ethyl acetate solution, are readily soluble even in ethyl acetate alone, and cannot be obtained in crystals from this solvent; on evaporating there results a very viscid, yellow, oily, ammonium salt, which gives oily precipitates, insoluble or sparingly soluble in water, with barium chloride and with the hydrochlorides of many organic bases. The *l*-menthylamine salt, prepared from it by precipitation, becomes pasty when cooled in a freezing mixture, but melts again at the ordinary temperature; after repeated fractional precipitation by water from its solution in well-cooled aqueous methyl alcohol or acetone, it is obtained as a flocculent mass which, when dried at 100°, melts indefinitely from 100—120° and appears to consist entirely, or for the most part, of the menthylamine salt of a benzylmethylethylpropylsilicanesulphonic acid, as shown by the following silicon determinations:

0·3918 gave 0·0530 SiO_2. Si = 6·4.
0·3341 ,, 0·0456 SiO_2. Si = 6·4.
$SiMeEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H,C_{10}H_{21}N$ requires Si = 6·4 per cent.

At first it seemed possible that the indefinite melting point and the badly defined character of this product was due to the partial resolution of the externally compensated sulphonic acid, but as the solution of the sodium salt obtained from it was found to show no optical activity, this view had to be reluctantly abandoned. Further attempts were then made to obtain some pure menthylamine salts from the mixture, and after a great deal of trouble this was finally accomplished in the following manner.

The various fractions of the menthylamine salt obtained from aqueous methyl alcohol are soluble in hot light petroleum (b. p. 50—60°), entirely, or to a very great extent; on adding a little water, stirring well, and then leaving in an ice-chest, some of the solutions deposit an oil, others a colourless, flocculent mass, or a nodular, indefinitely crystalline precipitate. After many extractions with wet light petroleum the oily deposit becomes very sparingly soluble and begins to crystallise; it is then carefully dried, dissolved in hot anhydrous acetone with the aid of a few drops of methyl alcohol, and the solution left over sulphuric acid; the salt, which then separates in gelatinous nodules, is finally obtained as a crystalline powder by deposition from boiling anhydrous acetone, and is described below (p. 733).

The flocculent, or nodular, deposits contain further quantities of the salt just referred to, and this is separated by systematic fractional crystallisation from wet light petroleum; the clear petroleum solutions then contain the greater part of the original sulphonation product in the form of menthylamine salts, one of which is a beautifully crystallised substance when pure, and almost insoluble in cold, wet petroleum, but which is only isolated with the greatest difficulty owing to the presence of some other substance, possibly an isomeride.

Details of this work are omitted because this crystalline substance, which is the *l*-menthylamine salt of benzylmethylethylpropylsilicanesulphonic acid, can be obtained in an infinitely simpler manner by another method (p. 739); it may be stated, however, that systematic fractional crystallisation from wet ice-cold light petroleum, combined with fractional crystallisation from ice-cold aqueous acetone, ultimately furnishes a small quantity of a pure substance melting at 122—123°, and there remain considerable quantities of fractions which are obviously mixtures, but which are so soluble in all ordinary solvents, except water, that they cannot be separated into their components.

It will, perhaps, be evident from the statements made that the sulphonation of benzylmethylethylpropylsilicane with sulphuric acid leads to the formation of a number of compounds in addition to the acids corresponding with the two salts which can be isolated; the nature of these by-products has not yet been investigated, but it seems probable that some of them are isomerides of the compounds described below, isomerism being due to the sulphonic group occupying a different position in the aromatic nucleus: this conclusion seems to be justified by the analytical results already given, which were obtained with specimens of salt which were certainly mixtures.

l-*Menthylamine Benzylethylpropylsilicolsulphonate*, $EtPrSi(OH)\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N$.

The compound which is so very sparingly soluble in light petroleum, and which is isolated from the sulphonation product of benzylmethylethylpropylsilicane in the manner already described (p. 732), is deposited from hot anhydrous acetone as a fine, crystalline powder; when exposed to moist air, while still containing acetone, it first becomes pasty, owing to absorption of water and then hard and crystalline again. It is almost insoluble in anhydrous ethyl acetate, but dissolves readily on adding a trace of water and warming; from this solution it is deposited in hydrated crystals which melt below 100° when rapidly heated. It is only very sparingly soluble in ether and in boiling water; hot aqueous solutions give, on cooling, glistening, microscopic plates. It dissolves freely in the common alcohols, and separates in rosettes of lustrous, poorly-defined prisms when the solutions are largely diluted with water. When dehydrated the salt melts at about 211—212°.

A sample crystallised from moist ethyl acetate was dried in the air:

0·4065 lost 0·0318 H_2O at 100°. $H_2O = 7·8$.

$C_{22}H_{41}O_4NSSi + 2H_2O$ requires $H_2O = 7·5$ per cent.

Analyses of the anhydrous salt gave the following results:

0·5391 gave 0·0734 SiO_2. Si = 6·4.
0·1667 „ 0·3647 CO_2 and 0·1386 H_2O. C = 59·7; H = 9·2.
0·1550 „ 0·3358 „ „ 0·1330 „ C = 59·7; H = 9·3.
0·1588 „ 0·3460 „ „ 0·1316 „ C = 59·5; H = 9·2.

The molecular weight of the salt was determined by the Landsberger modification of the ebullioscopic method in methyl-alcoholic solution; owing to the very small constant for this solvent the experimental error is abnormally high and the results are of little value; in fact with compounds of high molecular weight values differing by about 50 per cent. may be easily obtained:

Substance.	Solvent.	E.	M.W.
0·52	8·0 c.c.	0·16	437
1·03	11·5 „	0·25	385

The specific rotation was determined in 99·6 per cent. methyl-alcoholic solution; 0·443 substance; volume of solution 25 c.c.; 200 mm. tube; α −0·53°; $[\alpha]_D$ −15°.

The analytical results already given show that this salt is not what it was first thought to be, namely, a derivative of benzylmethylethylpropylsilicanesulphonic acid, for this compound would require C = 62·5, H = 9·7, and Si = 6·4 per cent.; they also exclude what otherwise might perhaps have been considered a possible view, namely, that the parent acid was derived from some homologue of benzylmethylethylpropylsilicane contained in the material sulphonated; such an impurity might conceivably have been present in small proportions and yet have escaped detection by analysis (compare p. 739).

The properties of this salt are also very different from those of *l*-menthylamine, benzylmethylethylpropylsilicanesulphonate (p. 735), so that the two compounds can hardly be homologous.

For these reasons the formula assigned to the salt above, which corresponds well with the analytical results, represents it as a derivative of benzylethylpropylsilicolsulphonic acid.

As the formation of such an acid cannot be attributed to the presence of benzylethylpropylsilicol in the original silicohydrocarbon (which had been repeatedly distilled with sodium) it may be assumed that hydrolysis occurs, as in the sulphonation of phenylbenzylethylpropylsilicane, possibly preceded by oxidation; the latter view would account for the evolution of sulphur dioxide which is invariably observed during the sulphonation of the silicohydrocarbon with sulphuric acid.

This interaction, as already stated, leads to the formation of several compounds, and the *l*-menthylamine salt in question is not only isolated with difficulty but is also produced in relatively very small quantities. In these circumstances, it did not seem worth while to examine the salt more fully in order to place its constitutional formula on a firmer basis.

When this sulphonation product was first obtained it was fractionally crystallised from various solvents in the hope of accomplishing its resolution; as these experiments were made with small quantities of material only and may not be very conclusive, they need not be described, and it will suffice to state that the melting point of the salt did not change appreciably; a solution of the sodium salt, prepared by expelling the *l*-menthylamine with sodium hydroxide, showed no appreciable rotation when examined in the polarimeter. Although fractional crystallisation failed to separate this salt into products differing in melting point, the author is not quite convinced of the homogeneity of the substance; it has in some respects the appearance of a mixture and may possibly contain some isomeride. The three combustions recorded above were made with three successive fractions obtained by crystallising from acetone, and as the menthylamine salt of benzylmethylethylpropylsilicanesulphonic acid is extremely soluble in this liquid, it is impossible that even traces of this salt could have been present.

l-*Menthylamine* dl-*Benzylmethylethylpropylsilicanesulphonate*, $MeEtPrSi\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N$.

The second pure compound ultimately isolated from the complex mixture of menthylamine salts obtained from the product of the sulphonation of benzylmethylethylpropylsilicane with sulphuric acid (p. 733) is very readily soluble in dry light petroleum (b. p. 55—65°) at the ordinary temperature, and does not separate even from highly concentrated solutions if moisture is excluded; when, however, a few drops of water are added, crystals soon form on the water globules, and if the petroleum is thoroughly wetted, the salt is deposited almost completely in highly lustrous, nacreous plates or in poorly-defined prisms. This behaviour is due to the combination of the readily soluble anhydrous salt with 2 molecules of water of crystallisation, as shown by the analyses of samples obtained in this way from wet petroleum and then dried in the air:

0·5835 lost 0·0430 H_2O at 100°; $H_2O = 7·37$.
1·3458 „ 0·1008 H_2O „ 100°; $H_2O = 7·49$.
$C_{23}H_{43}O_3NSSi + 2H_2O$ requires $H_2O = 7·54$ per cent.

Analyses of the salt dried at 100° until constant gave the following results:

0·1910 gave 0·4277 CO_2 and 0·1649 H_2O; C = 61·1. H = 9·6.
0·1933 „ 0·4416 CO_2 „ 0·1616 H_2O; C = 62·3. H = 9·3.
0·1850 „ 0·4233 CO_2 „ 0·1641 H_2O; C = 62·4. H = 9·9.
$C_{23}H_{43}O_3NSSi$ requires C = 62·5, H = 9·7 per cent.

As the substance contained both nitrogen and sulphur, the presence of which sometimes causes uncertainty in the results of elementary analysis, the composition of this salt was further established by boiling weighed quantities with excess of *N*/50 sodium carbonate solution and methyl alcohol until all menthylamine was expelled, and then titrating with *N*/50 sulphuric acid, using litmus as indicator; two experiments of this kind gave 441 and 440 as the equivalent of the salt, the calculated value being 441·4. Check determinations of the equivalent of menthylamine hydrochloride, which were made under exactly similar conditions, having given almost theoretical results, these determinations seemed to show, even more conclusively than the elementary analyses, that the salt had the composition assigned to it. Bearing in mind, however, the complexity of the original product of sulphonation, which indicated the occurrence of reactions other than mere substitution, it seemed desirable, later on, to determine the percentage of silicon in the salt in the usual way, namely, by heating with distilled sulphuric acid; the following results were thus obtained, the calculated percentage of silica being 13·7:

0·4636 gave 0·0545 $SiO_2 = 11·75$. 0·3495 gave 0·0413 $SiO_2 = 11·82$.
0·3738 „ 0·0423 $SiO_2 = 11·32$. 0·6981 „ 0·0827 $SiO_2 = 11·85$.

In these experiments a large quantity of sulphuric acid was used and a very deep platinum crucible, which was heated very cautiously, commencing at the top, but in spite of all precautions the results were far too low; whether this is due to particles of silica escaping with the other products of oxidation or to the formation of some volatile silicon compound it is difficult to say, but the latter conclusion seems the more probable; when the salt is carefully heated alone in a deep platinum crucible almost all the silica escapes, the residue being only about 2·5 per cent. of the weight taken; a similar behaviour was noticed in making the combustions of menthylamine benzylethylpropylsilicolsulphonate. Satisfactory silicon determinations cannot be made by the Carius method (the results are too high), but by carefully treating the salt with a large excess of fuming nitric acid and then heating, at first very cautiously, the following fairly good results were obtained:

0·2783 gave 0·0368 SiO_2 = 13·2.
0·3304 „ 0·0442 SiO_2 = 13·4.

l-*Menthylamine benzylmethylethylpropylsilicanesulphonate* is practically insoluble in water, but very readily soluble in ethyl acetate, carbon disulphide, and all ordinary organic solvents with the exception of wet light petroleum; it crystallises from aqueous acetone and aqueous methyl alcohol in flat plates, similar to those obtained from wet petroleum, and it does not seem to give massive, well-defined crystals very readily. When heated quickly, the hydrated salt melts rather irregularly at temperatures far below 100° (one of the facts which added to the difficulty of isolating it), but when very slowly heated it may be dehydrated without liquefying it, and the crystals then melt sharply at 122—123°. It is hydrolysed to a slight extent by boiling water, menthylamine being evolved, but it may be heated alone at a very high temperature without decomposing it to any great extent; it dissolves in fuming nitric acid with development of heat.

The physical properties of this and of other salts indicate that the parent acid is a simple substitution product of the silicohydrocarbon; a few molecular weight determinations which were made with the anhydrous menthylamine salt, in methyl-alcoholic solution by the ebullioscopic method, confirm this conclusion, but the results of experiments with acetone and with benzene show that in these solvents the molecules of the salt are highly associated.

Methyl Alcohol (ebullioscopic method).

Substance.	Volume of solution.	E.	M. W.
0·418	7·5 c.c.	0·200	299
1·146	11·5 „	0·425	265

Acetone (ebullioscopic method).

0·703	11 c.c.	0·135	1052
0·703	19 „	0·114	721

Benzene (cryoscopic method).

0·389	15 g.	0·055*	2316

* Depression of freezing point.

As already stated, the isolation of this *l*-menthylamine salt (m. p. 122—123°) is only successfully accomplished after a protracted course of fractional crystallisation; therefore, assuming that the parent acid is externally compensated, the salt ultimately obtained might be a derivative of one of the active components.

The polarimetric examination of anhydrous samples of the salt left this question undecided, as they could not be carried out in aqueous solution:

0·488 gram. Volume of solution, 25 c.c. 200 mm. tube; α −0·59°; $[\alpha]_D$ −15°;

0 685 gram. Volume of solution, 25 c.c. 200 mm. tube; α −0·83°; $[\alpha]_D$ −15·1°;

the solvent was 99·6 per cent. methyl alcohol.

The samples used in these determinations were decomposed with excess of potash, the menthylamine distilled in steam, and the solution of the potassium salt examined polarimetrically, but it showed no optical activity.

This result and facts given later show that the menthylamine salt is not derived from one optically active acid, and must therefore be regarded as a partially racemic substance; although, considering the numerous crystallisations it had already undergone, there seemed little prospect of being able to "resolve" it, a considerable quantity of the salt was repeatedly crystallised from aqueous methyl alcohol, the mother liquors from each operation being rejected; the specimen ultimately obtained when previously dehydrated melted at 122—123°, and gave the following result on polarimetric examination in 99·6 per cent. methyl-alcoholic solution:

0·6872 gram. Volume of solution, 25 c.c. 200 mm. tube; α −0·86°; $[\alpha]_D$ −15·6°.

Metallic Salts of dl-*Benzylmethylethylpropylsilicanesulphonic Acid.*

The examination of the metallic salts of benzylmethylethylpropylsilicanesulphonic acid has only been made very superficially, and chiefly with the object of obtaining one which could be easily purified, and which could then be used for silica determinations; this object, however, has not been attained. The *ammonium* salt remains as a buttery mass when its aqueous solution is evaporated, and is readily soluble in methyl alcohol and in cold ethyl acetate. The *sodium* salt is also very readily soluble in cold water, but on the addition of sodium carbonate and other salts it separates as a soapy mass, which on warming melts to an oil and then dissolves; when its solution evaporates spontaneously, it is deposited in crystalline leaflets. The *barium* salt is a buttery substance, practically insoluble in water, but like the barium salt of sulphobenzylethylpropylsilicol oxide is readily soluble in aqueous alcohol; the solution deposits an oil when it is allowed to evaporate.

The *calcium* salt is also oily, but soluble in water. The *lead* salt is sparingly soluble, but seems not to crystallise.

The acid itself and its simpler derivatives will form the subject of further investigation.

Sulphonation of Benzylmethylethylpropylsilicane with Chlorosulphonic Acid.

The extreme difficulty of isolating a pure substance from the product of the sulphonation of benzylmethylethylpropylsilicane, at any rate by the method described above (p. 732), rendered it necessary to discover some other method of preparation before the derivatives of the sulphonic acid could be examined in quantities suitable to the end in view; fortunately such a process was easily found, the sulphonation of the silicohydrocarbon with chlorosulphonic acid leading to excellent results.

Benzylmethylethylpropylsilicane (fraction b. p. 248—252°) is mixed with 3—4 volumes of dry chloroform, the solution cooled in ice, and a solution of chlorosulphonic acid in about 5 volumes of chloroform slowly added from a dropping funnel, shaking from time to time; the quantities are taken in accordance with the following equation as nearly as possible, a very slight excess of the acid rather than of the silicon compound being used:

$$SiBzMeEtPr + SO_3,HCl = SiMeEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H + HCl.$$

At first a slight reddish-brown coloration is produced, and towards the end of the operation a fairly vigorous evolution of hydrogen chloride sets in; the interaction seems to take place very rapidly, with formation of the sulphonic acid (and not the sulphochloride) and is at an end as soon as the whole of the chlorosulphonic acid has been added

The solution is then poured on to ice, or into water, the chloroform separated by distilling in steam (the solution gives an emulsion with water) and the residual aqueous solution, which sometimes shows a violet fluorescence, treated with a faint excess of ammonia. After concentrating on the water-bath, the neutral solution of the ammonium salts is treated directly with *l*-menthylamine hydrochloride; at first there results, as is usual with these salts, a streaky, opalescent fluid resembling raw white of egg, but on adding a slight excess of the hydrochloride the menthylamine salt is precipitated in colourless crystals and can be separated by filtration.

It is thus possible to prepare this crude (but easily purified) salt in about as many minutes as it requires in hours, when the sulphonating agent is sulphuric acid.

The crude product is purified by recrystallisation from hot wet light petroleum (b. p. 55—65°) in which it is completely and readily soluble, and from which it separates on cooling in lustrous plates; the first deposits, when previously dried at 100°, melt from about 108—116°, but after three or four crystallisations, without much loss in weight, the melting point rises to and becomes constant at 122—123°. The petroleum mother liquors, worked up systematically, yield further quantities of the pure salt, then small crystalline fractions melting indefinitely from 100—120°, and finally a small quantity of a menthylamine salt which is very readily soluble in ice-cold wet petroleum and which solidifies to a waxy mass when free from solvent. The nature of the by-product contained in these more soluble fractions has not been investigated, but judging by its properties it is very closely related to the main product; possibly it is an isomeride, possibly a homologue derived from some small quantity of impurity in the silicohydrocarbon. The yield of pure hydrated salt is about 70 per cent. of the theoretical.

The *l*-menthylamine salt thus prepared is indistinguishable from the compound already described as *l*-menthylamine benzylmethylpropylsilicanesulphonate, obtained from the silicohydrocarbon by sulphonating with sulphuric acid; their identity was proved by melting point determinations made with the salts both separately and mixed together, and also by polarimetric observations.

The fact that the yield of pure salt is more than 50 per cent. of the theoretical excludes, of course, the possibility of it being derived from one of the active acids and it may be regarded therefore as partially racemic; the readiness with which the acid is formed from the silicohydrocarbon, the low temperature at which the reaction is carried out, and the comparative freedom from by-products, afford important and additional evidence that the acid is a simple substitution product of the parent compound.

In view of the difficulty of obtaining accurate determinations of the silicon in the salt (p. 736), the results by the usual method having indicated a molecular weight for the salt of about 500, its equivalent was again determined by the volumetric process previously employed (p. 736), freshly standardised solutions having been prepared; the result given was 443, the theoretical value being 441.

The *l*-menthylamine salt has been most useful during the whole investigation of this acid, just as was the corresponding salt of sulphobenzylethylpropylsilicyl oxide. It has served not only for the isolation and identification of the acid, owing to the readiness with which it crystallises and its well-defined character, but also as the starting point for the preparation of all the compounds described later; for the last purpose the pure compound is treated with a very slight excess of pure sodium carbonate and the liberated base distilled off in steam; during this process, as part of the menthylamine is displaced, the solution acquires the appearance and consistency of raw egg-albumen, becoming clear and mobile at the end of the operation; the solution of the sodium salt is then rendered faintly acid with acetic acid and evaporated on the water-bath.

Salts of Benzylmethylethylpropylsilicanesulphonic Acid.

Having obtained, by the methods described, a silicon derivative which was an externally compensated compound and at the same time a strong acid, the principal object for which it had been prepared seemed to be almost accomplished; to find some suitable salt which could be resolved by fractional crystallisation did not, in fact, appear to be a formidable task; the result of some months' work proved that the difficulty of this task had been underrated.

The d-*hydrindamine* salt is obtained as an oil on adding a solution of *d*-hydrindamine hydrochloride to a solution of the sodium salt of the sulphonic acid; it is only very sparingly soluble in water and does not crystallise even when kept for some days in an ice-chest; the l-*hydrindamine* salt has similar properties, but on mixing the two compounds the product, namely, the *dl*-salt, crystallises spontaneously.

The dl-*hydrindamine* salt, prepared by precipitating with *dl*-hydrindamine hydrochloride, is an oil at first, but it soon crystallises and separates from aqueous alcohol in lustrous, nacreous plates; these crystals melt below 50° if suddenly heated, but otherwise do not melt until about 130°; they are readily soluble in alcohol and aqueous acetone, practically insoluble in water. Only a small quantity of this salt was prepared, merely for the purpose of comparison with the salt of the *d*-base; the fact that the former crystallises readily whereas the later does not, may perhaps be taken as an indication of the externally compensated character of the siliconsulphonic acid.

The d-*bornylamine* salt was prepared by precipitation and obtained as a colourless oil which did not crystallise when kept in an ice-chest in contact with water; when, however, the oil was separated and dissolved in light petroleum it was ultimately deposited in fern-like crystals; as it was so very readily soluble in light petroleum and other organic solvents it did not appear to be of much use and was not further investigated.

The *brucine* salt and the *morphine* salt were both prepared in small quantities, but not investigated as they remained in an oily condition; possibly they may be obtained in crystals by methods found serviceable in other cases and their further examination is merely deferred.

Quinine Benzylmethylethylpropylsilicanesulphonate.[*]—The addition of an aqueous solution of quinine hydrochloride, $C_{20}H_{24}O_2N_2,2HCl + 2H_2O$, to a solution of the sodium salt of the silicanesulphonic acid gives at first a precipitate which dissolves on stirring, forming a viscid, streaky fluid; afterwards, the quinine salt is precipitated as an oil which soon solidifies to a very hard cake.

The product was washed with water, dried, and fractionally crystallised from a mixture of ethyl acetate and petroleum, from which it separated as a white powder; after many operations it was thus resolved into six fractions, all of which except the last (most soluble) melted simultaneously at about 165°.

Many other solvents were used for further fractional crystallisation, such as a hot mixture of benzene and light petroleum and cold aqueous methyl alcohol, but without bringing about any sign of the desired resolution.

The salt separates from aqueous or moist solvents in lustrous needles, which melt in their water of crystallisation if heated suddenly at 130°, but when heated slowly liquefy from 165—170°; from anhydrous solvents the compound is deposited in opaque nodules melting at 172—173°. It is readily soluble in alcohol, aqueous acetone, benzene, or ethyl acetate, but practically insoluble in water or light petroleum.

Quinine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—The normal salt, which has just been described, was treated with excess of hydrochloric acid in methyl-alcoholic solution, the alcohol evaporated, and the oily product, which soon solidified, washed with water; when dried, the crude salt melted at 198—203°.

It was first crystallised from aqueous methyl alcohol, then twice from aqueous acetone and separated into three fractions, but the first and last of these melted simultaneously at 204—205°. The most sparingly soluble portion was then roughly dried and dissolved in anhydrous acetone, from which it separated as a rather gelatinous precipitate; this was crystallised three times from anhydrous acetone, the salt becoming less and less soluble as traces of water were removed and the melting point rising to 207—208°. In spite of this slight difference in melting point the salt had not been otherwise changed; the most readily soluble fraction which melted indefinitely at about 198° was decomposed with sodium carbonate, and the filtered solution neutralised and precipitated with *l*-menthylamine hydrochloride; the resulting menthylamine salt, when crystallised from wet light petroleum, melted at 122—123° and appeared to be identical with the salt of the original silicanesulphonic acid.

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[*] As this and several other derivatives of the alkaloids were not analysed, the formula of the nitrogenous salt used as precipitant is given; these salts were all excellent preparations obtained from Merck.

Fractional crystallisation from ice-cold, aqueous methyl alcohol also failed to accomplish the desired result.

The crystals deposited from aqueous acetone and other solvents are but poorly defined; those obtained from aqueous solvents melt with effervescence when heated suddenly at 130° and immediately solidify again, so they probably contain water of hydration. The salt is readily soluble in the common alcohols or wet acetone, but only very sparingly so in anhydrous acetone.

Cinchonidine Benzylmethylethylpropylsilicanesulphonate.—The normal cinchonidine salt, obtained as a colourless solid on adding a solution of the hydrochloride, $C_{19}H_{22}ON_2,HCl + 2H_2O$, to a solution of the sodium salt of the sulphonic acid, has been examined very carefully.

The crude, air-dried substance, which melted at about 188°, was crystallised several times from aqueous methyl alcohol and then divided into three parts; except the most readily soluble one, which sintered at 189—190°, these melted sharply at 194—195°. The most sparingly soluble portion was then crystallised from aqueous acetone, from chloroform, and from a mixture of chloroform and petroleum, in the last case at as high a temperature as possible, but no change in melting point occurred.

After crystallising from ethyl acetate to get rid of dust, the specific rotation of this sample was determined in methyl-alcoholic solution, the salt having been dried at 100°:

0·5270 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha - 3{\cdot}03°$; $[\alpha]_D - 71{\cdot}9$.

This specimen was then crystallised five times on the water-bath from very dilute alcohol, the substance being deposited each time partly as an oil and partly crystalline; the most sparingly soluble fraction thus obtained was dried, recrystallised from ethyl acetate, and examined polarimetrically in methyl-alcoholic solution:

0·5916 solution. Volume of solution, 25 c.c. 200 mm. tube; $\alpha - 3{\cdot}42°$; $[\alpha]_D - 72{\cdot}3°$.

As this sample also melted at the same temperature as the original (once crystallised) salt it is obvious that it had not been resolved.

This cinchonidine salt is very readily soluble in methyl alcohol and separates from the aqueous solvent in lustrous, fairly well-defined prisms or needles melting at 194—195°; it also crystallises well from ethyl acetate, in which it is easily soluble on warming; it dissolves freely, in chloroform but is practically insoluble in light petroleum and in cold water.

Cinchonidine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—When the normal cinchonidine salt is dissolved in methyl alcohol, treated with excess of hydrochloric acid, and the solution evaporated, the hydrogen salt is deposited as an oil which soon solidifies; the washed, air-dried substance melts at about 220°.

It was first fractionally crystallised from aqueous methyl alcohol, then from aqueous acetone, and separated into three fractions, all of which melted at 220—222°. The most sparingly soluble portion was then roughly dried and crystallised three times from ethyl acetate; this sample, which melted at 220—222°, was dried at 100° and examined polarimetrically in methyl-alcoholic solution:

0·4518 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha -1{\cdot}82°$; $[\alpha]_D -50{\cdot}3°$.

The same specimen was then crystallised twice from ice-cold, aqueous methyl alcohol and five times from dilute aqueous methyl alcohol on the water-bath; under the latter conditions it was deposited partly solid, partly oily; finally it was dried, crystallised from ethyl acetate, and again examined in methyl-alcoholic solution:

0·5712 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha -2{\cdot}23°$; $[\alpha]_D -48{\cdot}8°$.

As this preparation still melted at 220—222°, it seemed obvious that no resolution had occurred, but in order to confirm this, the sample was decomposed with sodium carbonate, and the neutral solution of the sodium salt precipitated with *l*-menthylamine hydrochloride; the *l*-menthylamine salt was then crystallised from wet light petroleum and separated into two portions. Both of these, when dried, melted at about 120° and had all the properties of the salt of the original *dl*-sulphonic acid.

It may perhaps be added that the filtered solution of the sodium salt, obtained by decomposing the cinchonidine salt, is distinctly lævorotatory, owing to the presence of the alkaloid which is not completely precipitated.

The cinchonidine hydrogen salt crystallises well from aqueous methyl alcohol and aqueous acetone in long, lustrous needles; it is readily soluble in these liquids or hot ethyl acetate, but practically insoluble in water. It decomposes a little at about 220°, so the melting point depends to some extent on the rate of heating.

Cinchonine Benzylmethylethylpropylsilicanesulphonate.—This salt has also been examined very carefully. It is precipitated from a solution of the sodium salt on the addition of cinchonine hydrochloride, $C_{19}H_{22}ON_2,HCl + 2H_2O$, as an oil which soon solidifies.

The product was first extracted three times with boiling water, but only traces dissolved. It was then fractionally crystallised from aqueous acetone and separated into four approximately equal portions; the first and last deposits were then dried at 100° and examined polarimetrically in methyl-alcoholic solution:

0·4793 substance. Volume of solution, 25 c.c. 200 mm. tube; α +4·39°; $[\alpha]_D$ +113·7°.

0·7454 substance. Volume of solution, 25 c.c. 200 mm. tube; α +6·66°; $[\alpha]_D$ +111·7°.

These results, and the fact that the two samples melted simultaneously, having indicated that no resolution had occurred, the most sparingly soluble portion was next crystallised about five times from aqueous methyl alcohol, but its melting point did not change. The various fractions were therefore collected, dried, and crystallised about six times from anhydrous acetone so that ultimately the deposit formed only about 5 per cent. of the original salt; this was dried at 100° and examined in methyl-alcoholic solution:

0·7170 substance. Volume of solution, 25 c.c. 200 mm. tube; α +6·62°; $[\alpha]_D$ +115·4°.

It seems therefore that crystallisation from aqueous or from anhydrous solvents does not effect the resolution of this salt; the value $[\alpha]_D$ +111·7 obtained above with the most readily soluble portion is probably a little low, owing to the almost unavoidable presence of small quantities of impurity when the final mother liquors are evaporated almost to dryness.

The normal cinchonine salt crystallises well from very weak aqueous alcohol or acetone in highly lustrous needles which seem to contain water of hydration and melt at 87—90°; from hot anhydrous acetone, in which the salt is readily soluble, it separates in rather a gelatinous condition and then melts at 110—112°. It is readily soluble in cold ethyl acetate, methyl formate, or chloroform, from which solutions it is precipitated by light petroleum as a gelatinous mass which deliquesces on exposure to moist air.

Cinchonine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—When the normal salt just described is dissolved in methyl alcohol, treated with excess of hydrochloric acid, and the solution then evaporated or diluted with water, the hydrogen salt is deposited as an oil, which solidifies on cooling; the most sparingly and most readily soluble fractions of the normal salt previously referred to were separately converted into the hydrogen salt and the samples crystallised once from aqueous acetone; they melted simultaneously at 210—212° and had the same specific rotation within the limits of experimental error, confirming the conclusion that the normal salt had not been resolved.

The whole of the normal salt having been converted into the hydrogen salt, the latter was first extracted two or three times with warm water, in which it was practically insoluble, then dissolved in methyl alcohol and precipitated with water to the extent of about

95 per cent.; the salt from the filtrate was collected, dried, and examined polarimetrically in methyl-alcoholic solution:

0·3794 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha + 2·39°$; $[\alpha]_D + 78·7°$.

The rest of the salt was then roughly dried, dissolved in a little methyl alcohol, and the solution mixed with anhydrous acetone; on evaporating on the water-bath, adding fresh acetone from time to time, the salt separated in a somewhat gelatinous condition, and the hot solution was decanted; the residue was again dissolved in a very little methyl alcohol, acetone added, and the solution evaporated as before; these operations having been repeated several times, moisture is removed, and the salt finally separates from the boiling solution in long needles. A sample prepared in this way after five crystallisations was heated at 100° for a short time and examined in methyl-alcoholic solution, other conditions as before:

0·748 substance; $\alpha + 4·65°$, $[\alpha]_D + 77·7°$.

As this treatment proved ineffective, the whole of the salt was next crystallised from aqueous ethyl alcohol at the ordinary temperature; so long as the solution contained a moderate proportion of alcohol, the salt was invariably deposited as an oil, but on increasing the proportion of water it separated in lustrous needles. After about six crystallisations the most sparingly soluble fraction was dried and then extracted five times with hot acetone; the residue, after having been heated at 100°, was examined in methyl-alcoholic solution, other conditions as before:

0·6983 substance; $\alpha + 4·37°$; $[\alpha]_D + 78·2°$.

This fraction was then decomposed with ammonia, the solution filtered, evaporated until neutral, and precipitated with *l*-menthylamine hydrochloride; the *l*-menthylamine salt was identical in appearance and in melting point with the salt of the original *dl*-acid.

The cinchonine hydrogen salt decomposes slightly at its melting point and is practically insoluble in anhydrous acetone, but readily soluble in ethyl acetate, aqueous acetone, or the common alcohols.

Narcotine Hydrogen Benzylmethylethylpropylsilicanesulphonate.—The addition of a solution of narcotine hydrochloride, $C_{22}H_{23}O_7N,HCl$, to a solution of the sodium salt of benzylmethylethylpropylsilicanesulphonic acid produces an oily precipitate; as, at the same time, the solution acquires a very strong acid reaction, this precipitate probably contains the hydrogen salt. Wishing to obtain, in the first place, the normal salt, the solution was rendered faintly alkaline with ammonia, but this caused the separation of a powder which seemed to be either the alkaloid or a basic salt. The solution was therefore strongly acidified with hydrochloric acid and the addition of narcotine hydrochloride continued as long as a precipitate was formed; the product, at first an oil, soon solidified and was washed with dilute hydrochloric acid and then with water.

This substance, which may be regarded as the hydrogen salt, is very readily soluble in the common alcohols and in aqueous acetone, and separates again as an oil on adding water as long as there is a moderate proportion of the organic solvent present; if, however, dilution be carried so far that most of the salt is precipitated, and the oil is then stirred with a crystal of the salt it soon solidifies, and the liquid decanted from it gives a deposit of highly lustrous, slender needles when allowed to evaporate spontaneously.

The original product was treated in this way with much aqueous acetone and thus separated into seven fractions, of which the seventh (or residue) formed about 40 per cent. of the whole, only about 10 per cent. being contained in each of the six extracts; the deposits from the first and sixth extracts were then dried at 100° and examined polarimetrically in methyl-alcoholic solution:

I. 0·227 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha + 0\cdot72^\circ$; $[\alpha]_D + 39\cdot6^\circ$.

VI. 0·5839 substance. Volume of solution, 25 c.c. 200 mm. tube; $\alpha + 1\cdot90^\circ$; $[\alpha]_D + 40\cdot7^\circ$.

The melting point of the salt is indefinite; samples which have been kept over sulphuric acid for several days begin to melt at from 70° to 85° according to the rate of heating, and a similar behaviour is shown by specimens dried at 100°, at which temperature the salt is a colourless, very viscid oil.

Attempts to crystallise the salt from other solvents were unsuccessful; unlike all, or nearly all, the other alkaloidal salts of this acid, the narcotine salt seems soluble in anhydrous acetone as well as in ethyl acetate, and remained oily as long as any solvent was present; it was also precipitated as an oil on adding light petroleum to its solution in cold acetone.

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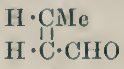
UNIVERSITY COLLEGE,
NOTTINGHAM.

LXIX.—*Electrolytic Reduction. Part III.*

By Herbert Drake Law.

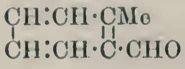
Electrolysis in Alkaline Solution.

In previous communications (Trans., 1906, **89**, 1512 and 1522) the reduction products of the aromatic aldehydes were studied, the work being confined almost entirely to alkaline solutions. From time to time complications were encountered, due to the formation of resinous substances which rendered the manipulation a matter of some difficulty. Although the appearance of these resins is a matter of frequent occurrence in the region of organic chemistry, very little attention has been devoted to their mode of formation. It became of interest, therefore, to systematise the results obtained by the electrolytic method, especially as this latter very closely resembles the natural process of resin formation. It has already been shown (Trans., 1905, **87**, 198; 1906, **89**, 1437) that the aldehydes which most easily resinify under the action of an electric strain contain an unsaturated carbon linking, and from this point of view the aromatic compounds must be regarded as a class intermediate between the saturated and unsaturated substances. Thus, benzaldehyde partially resinifies at the cathode when the high potential of such a metal as lead is employed. This is also the case with *p*-tolualdehyde and anisaldehyde, but with ortho (II) and meta (III) tolualdehydes complete resinification takes place even on platinum and nickel. The latter substances behave like true unsaturated compounds and may be compared with crotonaldehyde (I), which they closely resemble in structure:



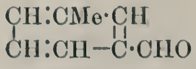
$$\begin{array}{l} H\cdot CMe \\ \;\;\;\;\;\| \\ H\cdot C\cdot CHO \end{array}$$

I.



$$\begin{array}{l} CH{:}CH\cdot CMe \\ |\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\| \\ CH{:}CH\cdot C\cdot CHO \end{array}$$

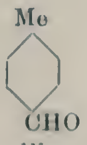
II.



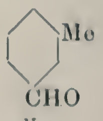
$$\begin{array}{l} CH{:}CMe\cdot CH \\ |\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\;\| \\ CH{:}CH-C\cdot CHO \end{array}$$

III.

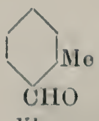
The combined influence of the groups $\cdot CHO$ and $\cdot CH_3$ tends to make the benzene nucleus an unsaturated aggregation, but this action will be felt only in an asymmetrical configuration. Thus, of the three tolualdehydes:



IV.

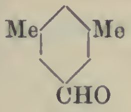


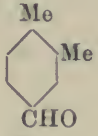
V.



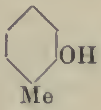
VI.

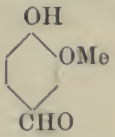
VI is the least symmetrical and most easily resinifies, whilst IV behaves like an ordinary ring compound. If we take V and VI and introduce a counter influence by means of another meta-substitution, a symmetrical arrangement may be arrived at with almost complete loss of tendency to resinify. Thus, from the compound

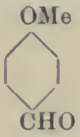

VII.

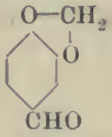

VIII.

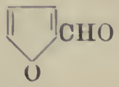
VII a well-defined crystalline substance may be obtained on reduction. By partly neutralising the effect of the grouping of VI by substitution as in VIII, an almost symmetrical compound is obtained and the product of the cathode chamber is mixed with 40 per cent. of resin. The groups OH, OMe, $O_2:CH_2$ also have a marked effect on the character of the benzene nucleus, as seen in the compounds

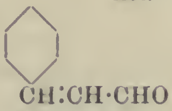

IX.


X.


XI.


XII.


XIII.


XIV.

IX gives non-crystalline substances unless the group OH is removed during the reaction; X is nearly symmetrical with respect to three influences, and gives a 50 per cent. yield of crystalline product in alkaline solutions. From XI crystalline substances alone were obtained, but XII resinifies in acid solutions; XIII is asymmetrical and unsaturated, and XIV is unsaturated, and both resinify with extreme ease. From this it seems quite clear that such groups which can bring about resinification when substituted in the benzene nucleus do so most readily when arranged so as to distort the whole molecule, a condition fulfilled with an asymmetrical grouping. The evidence is still incomplete, but it is hoped that in the future further developments may be made.

EXPERIMENTAL.

The apparatus used throughout this work differed only in detail from that already described (Trans., 1906, **89**, 1513), the principal change being the substitution of a porous pot of four times the capacity of that previously used, the cathodes being larger in proportion. A current density of 0·05 ampere per square centimetre was employed and maintained until the hydrogen absorption was complete, no account being taken of the voltage except as an indication of a resistance too high for efficient cooling. The cathodes were composed of either nickel or platinum—both polished—cut from sheets of the metal and bent in the form of cylinders. The solvent was a mixture of alcohol and water, and the electrolyte potassium hydroxide in sufficient quantity to be 5 per cent. of the total volume of liquid in the cathode chamber.

p-*Tolualdehyde.*—Twenty-six grams of this substance were dissolved in 200 c.c. of alcohol, to which was added 100 c.c. of water containing the necessary potassium hydroxide. A current of 4 amperes was passed through this mixture for four to five hours, at the end of which time 2280 c.c. of hydrogen had been absorbed, the theoretical quantity required for the production of hydrotoluoin being 2240 c.c. The solution was then poured in an excess of cold water, when a white, crystalline substance separated which weighed 26 grams. After being crystallised several times from alcohol this melted at 162—163°. The mother liquor was evaporated to dryness and the residue extracted several times with small quantities of cold alcohol, when a substance was obtained which melted at 126—127° after being once crystallised from benzene; the amount of each product was approximately 50 per cent. of the total. The substance melting at 162—163° gave the following results on analysis:

0·1004 gave 0·2910 CO_2 and 0·0680 H_2O. $C = 79·04$; $H = 7·52$.
$C_{16}H_{18}O_2$ requires $C = 79·33$; $H = 7·44$ per cent.

This substance was *hydrotoluoin* and was formed according to the following equation:

$$2C_6H_4Me·CHO + 2H = C_6H_4Me·CH(OH)·CH(OH)·C_6H_4Me.$$

A small quantity was dissolved in benzene, treated with phosphorus pentabromide, and allowed to stand for an hour. The benzene solution, together with the deposited crystals was removed from the unchanged phosphorus pentabromide and allowed to evaporate. After being crystallised from hot xylene, the product melted at 208° and was *p*-dimethylstilbene dibromide. This, on analysis, gave the following results:

0·2789 gave 0·2844 AgBr. $Br = 43·33$.
$C_{16}H_{16}Br_2$ requires $Br = 43·47$ per cent.

Many of the dibromo-derivatives of stilbene are not readily decomposed with fuming nitric acid, even on continued heating at high temperatures in sealed tubes, and as a consequence Carius's method cannot be employed for analysis. On heating these substances with a mixture of quicklime and sodium carbonate, complete decomposition takes place, and for this reason Piria and Schiff's method was used for the analyses.

The compound melting at 126—127° gave, on analysis, the following results:

0·1135 gave 0·3283 CO_2 and 0·0813 H_2O. C = 78·89 ; H = 7·92.
$C_{16}H_{18}O_2$ requires C = 79·33 ; H = 7·44 per cent.

This substance thus had the same composition as the above and was probably iso*hydrotoluoin.* On treatment with phosphorus pentabromide it gave dimethylstilbene dibromide, m. p. 208°, whereby its constitution is established. The dimethylstilbene dibromide obtained in these experiments is sparingly soluble in the alcohols, chloroform, benzene, toluine, or the paraffins. It crystallises from hot xylene in small, white plates which decompose at the melting point.

m-*Tolualdehyde and* o-*Tolualdehyde.*—In both these cases 6 grams of aldehyde were used in each experiment, 560 c.c. of hydrogen being therefore required for the complete conversion to hydrotoluoin. At the end of four hours this amount of reduction had taken place, but still an absorption of hydrogen continued slowly for a considerable period of time. The product was resinous and even on standing for several months deposited no crystals.

With methyl alcohol as solvent no improvement on the previous experiment was obtained. Sodium hydroxide was substituted for potassium hydroxide without any difference being detected. To reduce the resinifying effect of caustic alkalis, potassium acetate and carbonate were used as electrolyte, but the product was still non-crystalline and charred on distillation, even in a vacuum.

3 : 5-*Dimethylbenzaldehyde.*—Twenty grams were dissolved in 150 c.c. of alcohol, to which were added 80 c.c. of water containing the required amount of potassium hydroxide. The current was continued for five hours, at the end of which time complete reduction had taken place. The amount of hydrogen absorbed was rather less than that required by the equation: $2C_6H_3Me_2{\cdot}CHO + 2H =$

$$C_6H_3Me_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}C_6H_3Me_2.$$

The product was precipitated with water, as before, but contained a small amount of resin. This was removed with light petroleum and did not amount to more than 5 per cent. of the total product, the latter being almost the theoretical quantity. The separation of the two isomeric compounds was effected in exactly the same way as in the previous case, and two substances were obtained melting at 147—148° and 126—128° respectively. The compound of high melting point gave the following result on analysis:

0·2028 gave 0·5928 CO_2 and 0·1539 H_2O. C = 79·71 ; H = 8·43.
$C_{18}H_{22}O_2$ requires C = 80·00 ; H = 8·15 per cent.

This substance, on treatment with phosphorus pentabromide, gave a compound melting at 235° with decomposition. This was almost insoluble in the alcohols, chloroform, or the hydrocarbons. It crystallised best from hot xylene in colourless plates, which, on analysis, gave the following figures:

0·2164 gave 0·2070 AgBr. Br = 40·70.

$C_{18}H_{20}Br_2$ requires Br = 40·40 per cent.

The substance, then, is *tetramethylstilbene dibromide*,

$C_6H_3Me_2{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_3Me_2$,

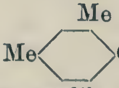
and the parent compound *hydroxyloin.*

The analysis of the substance melting at 126—128° yielded the following result:

0·1284 gave 0·3775 CO_2 and 0·0990 H_2O. C = 80·18; H = 8·56.

$C_{18}H_{22}O_2$ requires C = 80·00; H = 8·15 per cent.

This substance is iso*hydroxyloin*, having the same composition as the compound of higher melting point. This also yielded tetramethylstilbene dibromide on treatment with phosphorus pentabromide, m. p. 235°.

2:4-*Dimethylbenzaldehyde.*—This substance was prepared from ψ-cumene by a method previously described (Trans., 1907, 91, 258), but the constitution has never been accurately determined. It has been assumed to be  for the reason that a methyl group is attacked most readily in the ortho- and para-positions, and this is the only formula possible for the fulfilment of this rule. Ten grams were dissolved in 100 c.c. of alcohol, to which was added 50 c.c. of water and the required amount of potassium hydroxide. After passing the current through this mixture for four hours, rather less than complete absorption of hydrogen for the production of the compound $C_6H_3Me_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}C_6H_3Me_2$ had taken place. The solution was poured into water, when a semi-solid substance separated, which on standing for three weeks became crystalline. The quantity of solid matter obtained weighed 10 grams, but on being treated with light petroleum to remove the resin yielded only 6 grams of a crystalline substance. This was separated into two isomeric compounds melting at 153—154° and 129—130° respectively, the solvent used being a mixture of equal parts of benzene and light petroleum. The compound of higher melting-point gave the following result on analysis:

0·1239 gave 0·3635 CO_2 and 0·0950 H_2O. C = 80·01; H = 8·52.

$C_{18}H_{22}O_2$ requires C = 80·00; H = 8·15 per cent.

This substance is *hydroxyloin*; on treatment with phosphorus pentabromide, it yielded a compound readily soluble in benzene, but sparingly so in alcohol. On crystallisation from hot alcohol, this melted at 177—178° and gave, on analysis, the following result:

0·2182 gave 0·2100 AgBr. Br = 40·49.

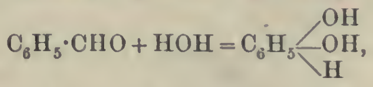
$C_{18}H_{20}Br_2$ requires Br = 40·40 per cent.

This was therefore *tetramethylstilbene dibromide.*

The substance melting at 129—130° was obtained in too small an amount for analysis, and was therefore converted into the dibromo-derivative as above. This melted at 177—178°, and was identical with tetramethylstilbene dibromide previously obtained, which proves the parent compound to be *iso*hydroxyloin.

Electrolysis in Acid Solution.

When sulphuric acid is used as an electrolyte very different results are obtained, primary alcohols, unsaturated and saturated hydrocarbons complicating what was in the first case a simple reaction. Apart from this, temperature has a great influence on the reducing action in acid solution, a fact which is almost absent when using alkalis. In this connexion an apparent anomaly is encountered. At the ordinary temperature the chief product obtained from an acid solution is a primary alcohol. Thus, from benzaldehyde a good yield of benzyl-alcohol may be obtained. As the temperature rises, however, the percentage yield of the latter product decreases, and the crystalline, mixed hydrobenzoins take its place. In other words, the least amount of reduction takes place at the higher temperature. To account for these curious results the products of reduction of a large number of well defined aromatic aldehydes were studied. It has been assumed that caustic alkalis react with these aldehydes, and in support of this view many facts may be brought forward as evidence, one of the most striking being the ready solubility of benzaldehyde in potassium hydroxide solutions containing small quantities of alcohol. The following equation probably represents this change:



$$C_6H_5\cdot CHO + HOH = C_6H_5\left\langle\begin{matrix}OH\\OH,\\H\end{matrix}\right.$$

the compound formed being readily reduced owing to the presence of two hydroxyl groups attached to one carbon atom. At the ordinary temperature dilute sulphuric acid does not exhibit the same tendency to react with the aldehyde. When reduction takes place the double link is broken, forming the substance $\cdot RCH\cdot O\cdot$, which immediately unites with hydrogen to form $RCH_2\cdot OH$. At the same time the junction of two radicles, $\cdot RCH\cdot OH$, is prevented by the close proximity of the carbon and oxygen.

It is possible, however, to break both links and completely remove the oxygen and so destroy its influence. In the latter case we may have:

$$\mathrm{RCH}{:} \longrightarrow \mathrm{RCH{:}CHR},$$
$$\mathrm{RCH}{:} + \mathrm{H} \longrightarrow \mathrm{RCH_2} \longrightarrow \mathrm{RCH_2{\cdot}CH_2R},$$
$$\mathrm{RCH_2}{\cdot} + \mathrm{H} \longrightarrow \mathrm{RCH_3},$$

or from benzaldehyde we may obtain stilbene, toluene, or dibenzyl.

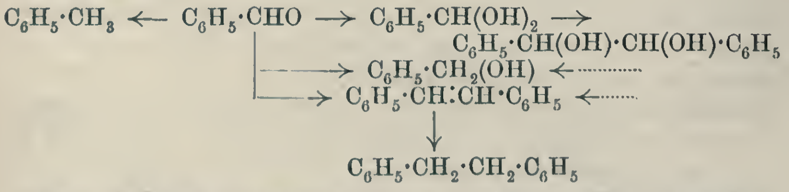
The two former were identified in the reaction product, and the latter was probably also present. As the temperature of the acid mixture increases, however, the reaction between the benzaldehyde and the sulphuric acid makes itself more and more apparent, and derivatives of the dihydric alcohol are probably formed:

$$\mathrm{RCHO} + \mathrm{H_2O} = \mathrm{RCH(OH)_2}.$$

Thus, as in the case of alkaline solutions, the close proximity of the oxygen and carbon atoms has been destroyed and readily reducible compounds formed. The reduction then proceeds in the following manner:

$$\mathrm{RCH(OH)_2} + \mathrm{H} \longrightarrow \mathrm{RCH(OH)}{\cdot} \longrightarrow \mathrm{RCH(OH){\cdot}CHR(OH)}.$$

The complete course of the reaction may be represented in the following scheme:



The dotted lines represent a very slow reaction. This is analogous in every way to the reduction of the nitro-compounds, and takes place with almost all the aldehydes examined, exceptions being met with in the cases of salicylaldehyde, vanillin, and piperonaldehyde, which resinify.

Benzaldehyde.—These experiments were conducted in exactly the same manner as those already described, the only modification being the substitution of 5 per cent. sulphuric acid for the caustic alkali, and sheet copper for the cathode material. The latter was cut from sheets of the electrolytic metal and cleaned by means of nitric acid and fitted as before. In each case the current density employed was 0·05 ampere per square centimetre. The whole apparatus was surrounded by a large glass vessel to serve either as a cooling or heating apparatus. Twenty-six grams of benzaldehyde were dissolved in 150 c.c. of alcohol, to which was added 100 c.c. of water containing the required amount of sulphuric acid. A current of 4 amperes was continued for five and a half hours, and the temperature was regulated as nearly as possible to that required. The whole product was precipitated with water and allowed to stand overnight. The crystals were separated by filtration, and the oil extracted with ether and fractionated. In this manner the following fractions were obtained; I, 0—100°; II, 160—250°; III, 280—320°. Fraction I was washed with water to remove any alcohol and carefully refractionated and finally identified as benzene. Fraction II contained a little unchanged benzaldehyde, which was removed by treatment with sodium bisulphite, the remainder being benzyl alcohol, b. p. 206°. The portion boiling above 250° solidified on cooling and contained mixed hydrobenzoins, a product boiling at 306°, and small quantities of substances not identified. The compound of boiling point 306° solidified on cooling and crystallised readily from alcoholic solutions in large thin plates, m. p. 124°. This substance rapidly absorbed bromine in chloroform solution without the liberation of hydrogen bromide and the product melted at 237° with decomposition, after being crystallised from hot xylene. It was almost insoluble in the ordinary organic solvents, and, on analysis, gave the following results:

0·2700 gave 0·3000 AgBr. Br = 47·26.

$C_{14}H_{12}Br_2$ requires Br = 47·06 per cent.

From this it may be concluded that the compound is stilbene dibromide and the parent substance stilbene. The product not distilling below 330° was small and was not treated further. From three experiments, conducted at different temperatures, the following results were obtained:

Benzaldehyde taken.	Temperature.	Hydrobenzoins.	Benzyl alcohol.	Stilbene.	Benzene.
26 grams	5°	6 grams	9 grams	3–4 grams	1 gram
26 ,,	17	8–9 ,,	5–7 ,,	3-4 ,,	1 ,,
26 ,,	34	15 ,,	3–4 ,,	3–4 ,,	1 ,,

Hydrobenzoins.—Pure hydrobenzoin is not sufficiently soluble in alcohol and water to permit the treatment of more than 2—3 grams at a time. It was slowly attacked by electrolytic hydrogen, the products being benzyl alcohol and stilbene. The crude product obtained by reduction in alkaline solution contained small quantities of resin and was readily soluble in a mixture of alcohol and water, but in this state it is not readily reduced in acid solution. The experiments had to be stopped at this point, but it is hoped that they may be continued in the near future.

p-*Tolualdehyde.*—Twenty-four grams were dissolved in 180 c.c. of alcohol, to which was added 100 c.c. of water containing the required amount of sulphuric acid. The absorption of hydrogen proceeded rapidly at first, but more slowly after two hours, and was still progress-ing slowly after six hours, probably due to the secondary reactions. At the end of this time 3320 c.c. of hydrogen had been absorbed, whilst the equation $C_6H_4Me{\cdot}CHO + H = C_6H_4Me{\cdot}CH_2{\cdot}OH$ requires 4480 c.c. The product was poured into water and treated as in the previous case. The following fractions were obtained: I, 0—120°; II, 150—250°; III, 300—330°, and in addition to this a small amount of residue was left in the flask. I was washed with water and fractionated, giving a liquid boiling at 110°, which was proved to be toluene. II was refractionated and a product obtained boiling constantly at 216°, which solidified on cooling and melted at 59°; this was *p*-xylyl alcohol. III was refractionated and the bulk distilled at 320—330° and solidified in the receiver. On crystallisation from alcohol a compound was obtained melting at 176°. This substance rapidly absorbed bromine from chloroform solution and deposited a substance melting with decomposition at 208°.

This substance is *p*-dimethylstilbene dibromide and the parent compound is dimethylstilbene. The above aldehyde is affected in precisely the same manner as the previous one when electrolysed at different temperatures and the results of two experiments may be tabulated as follows:

Aldehyde taken.	Temperature.	Hydrotoluoins.	Xylyl alcohol.	Dimethylstilbene.	Toluene.
24 grams	14°	6 grams	10 grams	4 grams	1 gram
,,	35	13 ,,	4 ,,	4 ,,	1 ,,

m-*Tolualdehyde.*—Twenty grams were dissolved in a mixture of alcohol (180 c.c.) and water (80 c.c.) and the required amount of sulphuric acid. A current of 4 amperes was passed through this mixture for five to six hours, at the end of which time 3520 c.c. of hydrogen had been absorbed whilst 3740 c.c. were necessary for the complete reduction to *m*-xylyl alcohol. The product was precipitated with excess of water and extracted with ether. After evaporating the ether the following fractions were obtained: I, 0—160°; II, 170—230°; III, 300—333°. I gave *m*-xylene on refractionation and this was identified by qualitative tests. Yield 1—2 grams. II yielded a fraction boiling at 217°, which constituted the main product of the reaction. This was *m*-xylyl alcohol. Yield 14—15 grams. III was carefully refractionated and a substance was isolated boiling at 320—330°. This, however, could not be obtained in a pure state. It readily absorbed bromine and yielded a crystalline product. To a solution in chloroform, therefore, a slight excess of bromine was added and the mixture was allowed to evaporate in the air. The crystalline residue was dried in a porous plate to remove the adhering oil, and finally crystallised from alcohol and benzene. This substance is sparingly soluble in the alcohols, but readily so in the benzene hydrocarbons. It melts at 164—165° and an analysis gives the following result:

0·1817 gave 0·1860 AgBr; Br = 43·74.

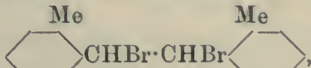
$C_{16}H_{16}Br_2$ requires Br = 43·47 per cent.

This is *dimethylstilbene dibromide* and the amount obtained corresponds to 2 grams of dimethylstilbene. The mixture obtained above consists of this substance and probably toluoin, but a sufficient quantity was not obtained to enable work to be continued in this direction.

o-*Tolualdehyde.*—Twenty grams of this substance were treated in exactly the same manner as the previous one. In six hours the reduction was almost completed, but only 2440 c.c. of hydrogen had been absorbed. The product was treated as before; the following fractions were obtained: I, 0—170°; II, 100—160°/30 mm.; III, 200—300°/30 mm. The first fraction consisted of 1—2 grams of *o*-xylene and was identified by means of qualitative tests. The boiling point of fraction II was 135° at 30 mm., and this was found to be *o*-xylyl alcohol. Yield 6 grams. III weighed 10 grams, and was by far the largest portion. On standing it deposited 5 grams of a white, crystalline substance. This was crystallised from a mixture of benzene and light petroleum and a product obtained melting at 173—176°. It probably still contained traces of impurities, but the amount was too small to perform further experiments. The mother liquors were concentrated and a benzene solution was treated with phosphorus pentabromide. Dense clouds of hydrogen bromide were liberated and a crystalline product was obtained from the benzene solution. The crystalline solid was readily soluble in benzene, but dissolved with difficulty in light petroleum and alcohol. From the latter solvent it was obtained in small needles melting at 173—174°. On analysis:

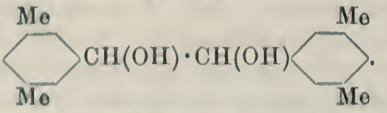
0·2040 gave 0·2040 AgBr. Br = 43·31.

$C_{16}H_{16}Br_2$ requires Br = 43·47 per cent.

This substance was *dimethylstilbene dibromide*, having the constitution , and the parent compound was a mixture of isomeric hydrotoluoins. The non-crystalline residue obtained from III was dissolved in chloroform and treated with bromine, which it absorbed very readily, but shortly liberated dense clouds of hydrogen bromide. The solution was allowed to evaporate, but did not deposit any crystals. It was therefore dissolved in light petroleum and allowed to stand for a few days, when a crystalline product was deposited. After recrystallisation from alcohol, this was identified as dimethylstilbene dibromide, melting at 173—174°. The parent substance was *o*-dimethylstilbene. The remaining substance was resinous and could not be identified. In the above experiment the temperature was allowed to rise to 20°, which accounts for the small yield of *o*-toluyl alcohol.

2 : 4-*Dimethylbenzaldehyde.*—Twenty grams of this substance were treated at 13° in exactly the same manner as the previous aldehyde. The product was fractionated under reduced pressure and at 30 mm. the following portions were obtained: I, 0—140°; II, 140—200°; III, 250—270°. Fraction I consisted of *ψ*-cumene and was identified by qualitative test. Yield 1—2 grams. Fraction II constituted the bulk of the product and was *ψ*-cumyl alcohol, b. p. 232°. Yield 14—15 grams. The fraction distilling at 250—270° did not solidify on standing. It was dissolved in chloroform and treated with bromine as in the previous cases. The reaction mixture did not crystallise on evaporation, and was therefore dissolved in light petroleum and allowed to stand for some days. At the end of this time crystals had separated, which were washed with light petroleum and finally recrystallised from alcohol. The product melted at 177—178° and was identical with tetramethylstilbene dibromide previously obtained. The quantity obtained corresponded to 0·5 gram of tetramethylstilbene, but the whole mass contained so much resinous matter that accurate determinations could not be made.

3 : 5-*Dimethylbenzaldehyde.*—Twenty grams of this substance were treated as in the previous case. After passing a current of 4 amperes through the mixture for four to five hours only half the amount of hydrogen necessary for the conversion of the aldehyde into the alcohol had been absorbed. The reaction was not complete and proceeded slowly for three to four hours more. The temperature was 15° during the whole experiment. The product was fractionated under a pressure of 30 mm. and the following portions were obtained: I, 0—140°; II, 140—200°; III, 250—270°. Fraction I consisted chiefly of mesitylene and was identified by the usual qualitative tests. Yield 1—2 grams. II constituted the bulk of the product and was mesityl alcohol b. p. 220°. Yield 14—15 grams. Fraction III weighed 4 grams and on standing solidified partly. This portion was removed from the resinous matter by washing with light petroleum and was crystallised from a mixture of benzene and light petroleum. Yield 1 gram. The final product melted at 147—148°, and was probably *iso*hydroxyloin, having the constitution,



This was treated with phosphorus pentabromide, and tetramethylstilbene dibromide, was obtained, melting at 235°. This proves conclusively the correctness of the above view. The resin was treated with bromine and the product allowed to evaporate to dryness. The sticky mass was dissolved in light petroleum and allowed to stand. In this manner crystals were obtained which on purification melted at 235° and were identified with tetramethylstilbene dibromide. The amount obtained corresponded to 1·0—1·5 grams of tetramethylstilbene, the latter not being isolated in a pure state.

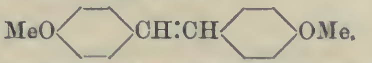
Salicylaldehyde, Piperonaldehyde and Vanillin.—These substances all resinified on electrolysis. The product obtained from salicylaldehyde resembled in appearance and fracture ordinary resin. None of these resins could be distilled, even under reduced pressure, owing to abnormal frothing.

Anisaldehyde.—Twenty grams of this substance were dissolved in a mixture of 200 c.c. of alcohol, 100 c.c. of water, and the required amount of sulphuric acid. A current of 4 amperes was employed and the temperature kept below 14°. At the end of five hours sufficient hydrogen had been absorbed to convert the whole into anisic alcohol. The product was recovered as before and finally allowed to stand in a vacuum desiccator for some days, when crystals separated which were collected. The residue was fractionated under reduced pressure. The bulk of the product distilled at 120—200° at 30 mm. pressure, but a substance was obtained between 250° and 260° at 30 mm. pressure which solidified in the receiver. This was added to the first crystalline product, the total weight being 2—3 grams. This substance was almost insoluble in the alcohols, but dissolved slightly in ethyl acetate or hot benzene. On crystallisation from the latter it melted at 213—214°. On analysis:

0·1245 gave 0·3641 CO_2 and 0·0737 H_2O; C = 79·76; H = 6·57.

$C_{16}H_{16}O_2$ requires C = 80·00; H = 6·67 per cent.

This substance was *dimethoxystilbene*,



It readily decolorised a chloroform solution of bromine and formed a substance almost insoluble in all the ordinary organic solvents. From a large excess of xylene it was obtained in colourless needles or small plates melting at 180° with decomposition. The analysis gave the following result:

0·2121 gave 0·2018 AgBr. Br = 40·45.

$C_{16}H_{16}O_2Br_2$ requires Br = 40·00 per cent.

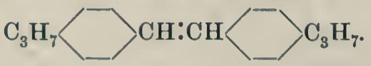
This was *dimethoxystilbene dibromide.* The fraction boiling at 120—200° was redistilled and identified as anisic alcohol, boiling at 259°/760 mm. Yield 14—15 grams. From the lowest fraction anisole was isolated as in the previous cases. Yield 1 gram. The small residue of the mixed hydroanisoins was not investigated further. At higher temperatures a good yield of mixed hydroanisoins was obtained; these have been investigated previously (*loc. cit.*).

Cuminaldehyde.—Twenty-five grams of this substance were dissolved in 200 c.c. of alcohol and 100 c.c. of water and sulphuric acid, and subjected to the reducing action of the current for six hours at 20°. At the end of this time sufficient hydrogen had been absorbed to convert the aldehyde into the alcohol. The product was treated as in the previous case. The following fractions were collected: I, 0—120°; II, 155—175°; III, 240—265°, in each case the pressure being 35 mm. I was washed with water and refractionated. The product had the characteristic sweet odour of cymene and boiled at 175°. Yield 2 grams. II, on being distilled at the ordinary pressure, boiled chiefly at 246°, and was cuminyl alcohol. Yield 13—15 grams. Fraction III solidified on standing in the receiver and was washed with alcohol, from which it was finally crystallised. This substance forms large plates melting at 131—132°, sparingly soluble in the alcohols but more readily so in chloroform or the aromatic hydrocarbons. On analysis:

0·1120 gave 0·3730 CO_2 and 0·0963 H_2O. C = 90·83; H = 9·55.

$C_{20}H_{24}$ requires C = 90·91; H = 9·09 per cent.

This substance is *di*iso*propylstilbene,* having the constitution



It absorbs bromine rapidly from chloroform solution, and in evaporation leaves a deposit almost insoluble in the alcohols, sparingly soluble in chloroform and readily so in the hot aromatic hydrocarbons. It crystallises from benzene in needles or small plates melting at 213—214° with decomposition. On analysis:

0·2300 gave 0·2020 AgBr. Br = 37·37.

$C_{20}H_{24}Br_2$ requires Br = 37·73 per cent.

The substance is *di*iso*propylstilbene dibromide.* The yield of parent substance was 2 grams, but more remained in a form which would not crystallise. The hydrocuminoins present were not isolated. An increase of temperature had exactly the same effect as in the previous cases.

In conclusion I wish to express my thanks to the Government Grant Committee of the Royal Society for partly defraying the expenses of this research.

BOROUGH POLYTECHNIC, S.E.

LXX.—*The Estimation of Small Quantities of Nitrogen Peroxide.*

By ROBERT ROBERTSON, M.A., D.Sc., and SIDNEY SCRIVENER NAPPER.

THE following method was worked out primarily for the purpose of following the evolution of nitrogen peroxide in the decomposition of explosives, but is equally applicable to other gaseous mixtures where this gas is present in small proportions.

It is based upon the characteristic absorption spectrum of nitrogen peroxide, which consists of a large number of fine dark lines extending throughout the visible spectrum and a general absorption strongest in the violet and diminishing gradually as it approaches the red end.

It was found that the lines could be distinguished in very dilute mixtures of nitrogen peroxide and carbon dioxide or air, a few of the more prominent groups of lines being still visible at a concentration as low as 0·05 per cent. of nitrogen peroxide. As the proportion of nitrogen peroxide was raised the lines increased in intensity and number, and in mixtures approaching 1 per cent. the violet end of the spectrum was completely absorbed. These differences were sufficiently well marked to enable one to estimate the concentration by comparison with standard mixtures to within 0·02 per cent. in the case of the more dilute mixtures and 0·05 per cent. in the case of the stronger ones.

For the sake of convenience, greater accuracy and the elimination of the personal equation as far as possible, it was decided to make photographic records in cases where quantitative results were desired. For this purpose a series of standard photographs covering a range of concentration of nitrogen peroxide from 0·5 to 1 per cent. was prepared.

Preparation of Standard Photographs.—The spectroscope was a Hilger No. 1 table spectroscope with a single dense flint glass prism. It was provided with a camera attachment, which allowed seven photographs to be taken on a $3\frac{1}{4}''$ by $2\frac{1}{8}''$ plate. The Ilford chromatic plate was found most suitable on account of its fine grain, freedom from fog, and the convenience of being able to use a fairly bright dark-room light.

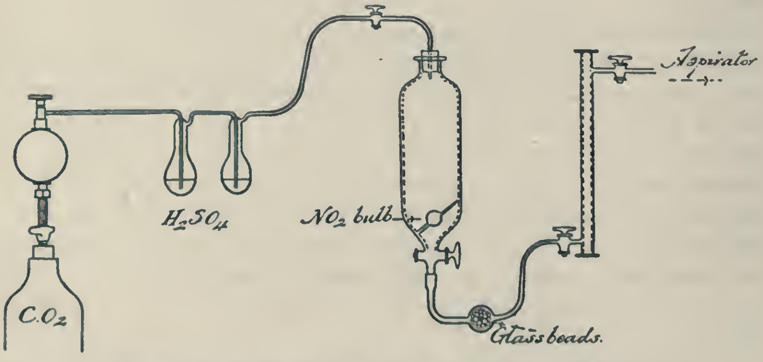
A Welsbach incandescent mantle was used as the source of light.

The vessel for containing the gas under observation was a straight glass tube 40 cm. long with side tubes provided with stopcocks. The ends were closed by glass discs, attached by means of a cement.

Owing to the small volume of the tube and the low concentration of the nitrogen peroxide it was found necessary to make the mixture in a large vessel and then to fill the observation tube. Small glass bulbs of capacity from 0·5 to 12 c.c. with two capillary ends were filled with nitrogen peroxide at atmospheric pressure from a U-tube, in which it had previously been liquefied. In some cases the capillary tubes were quickly sealed with a small blow-pipe flame, and in others simply closed by holding the bulb by the tubes between the fingers before dropping it into the large cylinder which had been filled with dry carbon dioxide.

The bulb was then broken by shaking the cylinder, and when diffusion was complete from one-third to one-half of the gas was aspirated through the observation tube (Fig. 1). A small trap containing glass beads was interposed to prevent pieces of broken glass from the bulb being carried over and deposited on the flat ends of the tube, where they were found to interfere with the passage of light. The stopcocks were then closed and the absorption spectrum of the gas was photographed.

FIG. 1.



Apparatus for preparing standard mixtures of CO_2 *and* NO_2.

The direct light from the mantle was shielded by a screen of thin sheet copper with a circular aperture which allowed the light to pass through the tube to the spectroscope.

The source of light and the slit of the spectroscope were 15 cm. and 1 cm. distant from their respective ends of the tube. The slit was closed down to 0·05 mm., and under these conditions an exposure of forty seconds was sufficient, although as a rule several different exposures were given to allow for slight variations in the negatives with which the standards were to be compared.

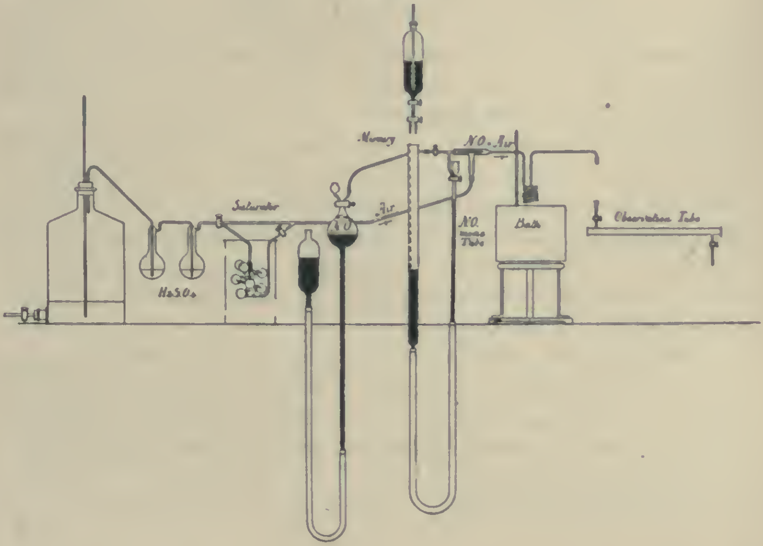
The plates were developed in the Ilford pyro-soda developer, using the full quantity of pyrogallic acid but no potassium bromide.

The composition of the gaseous mixtures used in the preparation of the standard photographs was calculated on the assumption that the nitrogen peroxide would be dissociated into NO_2 at the degree of dilution used in these experiments. The gas was measured at 27°, and its composition was taken to be 80 per cent. of N_2O_4 and 20 per cent. of NO_2 (Deville and Troost, *Jahresb.*, 1867, 177).

Photographs were taken of the mixtures of nitrogen peroxide and carbon dioxide referred to on p. 761, and these photographs are reproduced in Fig. 2 (see plate facing p. 775).

Application to the Estimation of Traces of Nitrogen Peroxide in Air.—In studying the effect of water vapour on nitrogen peroxide in connexion with the decomposition of explosives, an apparatus was devised for the production of mixtures of two gases in definite proportions, which were then passed through a tube and examined with the spectroscope. Advantage was taken of this to prepare a series of mixtures of air with small quantities of nitrogen peroxide. The apparatus used for this purpose is shown in Fig. 3.

FIG. 3.



A slow steady current of nitrogen dioxide was obtained by dropping a very fine stream of mercury into the compensating tube of a gas burette connected to a capillary tube. This slow current of nitrogen dioxide was blown through the capillary tube into a comparatively faster stream of dry air, the rate of which had been measured by passing it through two gas washing bulbs of sulphuric acid. The nitrogen dioxide became oxidised to nitrogen peroxide on coming in contact with the air, and the absorption spectra of the mixtures were photographed, the proportion of nitrogen dioxide present being estimated by comparison with the set of standard photographs of absorption spectra of nitrogen peroxide in carbon dioxide.

Experiment.	Rate of NO c.c. per hour.	Rate of air c.c. per hour.	Concentration of NO_2 in air, calculated from NO used.	Concentration by comparison of photographs with standard photographs of NO_2 in CO_2.
1	3·00	1970	0·0015	0·0013
2	2·40	1020	0·0023	0·0020
3	2·40	690	0·0034	0·0027
4	5·40	1020	0·0052	0·0045
5	4·80	410	0·0114	0·0095

The results given in the preceding table show that the concentrations found by the method described in the present paper agree very fairly with those actually present.

It will be observed that the concentration of nitrogen peroxide as arrived at from the spectroscopic comparison is slightly lower in all cases than that calculated from the proportion of nitrogen dioxide used. This is possibly due to the fact that a distinct interval of time in seconds is required for the formation of nitrogen peroxide in this manner, as is shown by Raschig (*Zeitsch. angew. Chem.*, 1905, **18**, 1281) and Lunge (*ibid.*, 1906, **19**, 861).

An extended trial of the method has proved it to be trustworthy and capable of employment in practically all cases where nitrogen peroxide is present in small quantity, and it has been successfully used in the investigation of the gaseous products of decomposition of explosives.

Royal Gunpowder Factory,
Waltham Abbey.

LXXI.—*The Evolution of Nitrogen Peroxide in the Decomposition of Guncotton.*

By Robert Robertson, M.A., D.Sc., and Sidney Scrivener Napper.

Introduction.

In studying the nature of the gaseous products evolved during the decomposition of explosives, the quantitative determination of the nitrogen peroxide present is of great importance.

The presence of this gas is indicated both by the reactions of the so called "trace methods" such as the Abel heat test, the diphenylamine test of Guttmann and Hoitsema and the *m*-phenylenediamine test of Spica, and by the observation of red fumes in some well-known tests, for example, those of Simon Thomas (*Zeitsch. angew. Chem.*, 1898, 1027) and of Sy (*J. Amer. Chem. Soc.*, 1903, **25**, 549), &c.

In none of these tests is a quantitative estimation made of the nitrogen peroxide present, and in a few cases where there has been an attempt to estimate the extent to which this gas exists, the statements made are unsatisfactory.

Thus, Hoitsema (*Zeitsch. physikal. Chem.*, 1898, **27**, 567), in an investigation on the products of decomposition of guncotton in a vacuum, collected the substance formed by the interaction of oxides of nitrogen and the mercury of the pump and calculated a figure for nitrogen peroxide from the reducing action of this substance on permanganate solution.

Again, Will in his "Untersuchungen über die Stabilität von Nitrocellulose," Zweite Mitteilung, p. 31, concludes that under the conditions of his test nitrogen dioxide is essentially the only volatile nitrogenous product of decomposition. It will be shown below that this is so far from being the case that, of the total nitrogen evolved during the performance of his test, a proportion of from 30 to 50 per cent. exists in the condition of nitrogen peroxide.

Further, in the results of the decomposition of nitrocellulose in a vacuum, given in the Report of the Chief of the Bureau of Ordnance (U.S.A.) for 1902, no mention is made of the presence of nitrogen peroxide.

To give still another example, in the analysis of the gases given off at 135° by nitrocellulose, A. V. Saposchnikoff and M. Borisoff state that nitrogen peroxide is evolved at the beginning of the reaction, but no figure showing the quantity present is given (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 836; *Abstr.*, 1904, i, 799).

As the quantity of nitrogen peroxide set free when the explosive is heated has an important bearing on the question of the stability of the material, the present investigation was undertaken to determine to what extent and under what conditions nitrogen peroxide is evolved during the decomposition of guncotton.

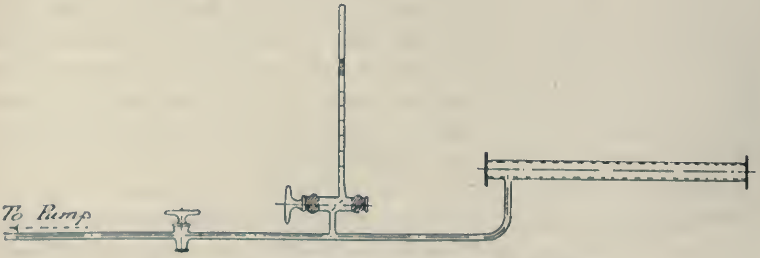
EXPERIMENTAL.

I. *Method.*—The method employed was that described by the authors in the preceding paper. This spectroscopic method was found to be specially suited to the estimation of traces of this gas in the gases evolved from decomposing guncotton. The estimation of the concentration of nitrogen peroxide is obtained by comparison of a photographic negative of the absorption spectrum of the gaseous mixture in question with a negative of a standard mixture of nitrogen peroxide. The concentration being thus obtained, the weight of nitrogen existing in this form in the mixture can be calculated.

II. *Preliminary Experiments on the Action of Water on Nitrogen Peroxide.*—The reaction of liquid and gaseous water with nitrogen peroxide is of special importance when the water which is produced as a normal decomposition product of the guncotton is not continuously removed from contact with the explosive. By the action of water in the liquid phase on nitrogen peroxide, nitrous and nitric acids are produced, and the conditions under which this takes place have been recently investigated by Lunge (*Chem. Zeit.*, 1904, 28, 1243).

Some experiments were performed on the action of water, both liquid and in the state of vapour, on nitrogen peroxide under conditions similar to those which occur in the experiments with guncotton described in this paper.

FIG. 1.



Apparatus for admitting liquid water to NO_2 *gas.*

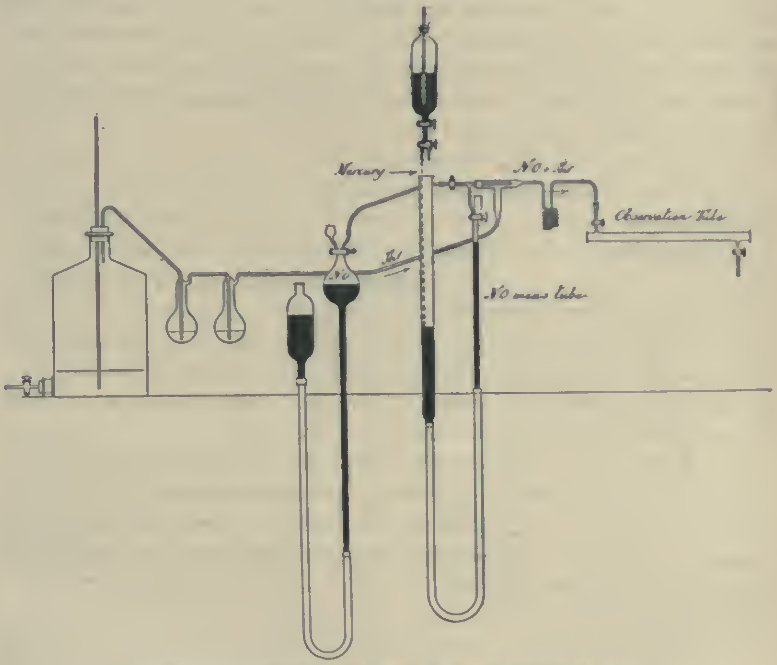
(a) *Effect of Water in Liquid Phase on Nitrogen Peroxide Existing in Small Concentration.*—An observation tube of 100 c.c. capacity was connected, on the one hand, to a vessel containing nitrogen peroxide and, on the other, to a narrow graduated tube fused on to a stop-cock, as in Fig. 1.

In one experiment, sufficient nitrogen peroxide was admitted to the evacuated observation tube to give a spectrum corresponding to 0·25 per cent. of nitrogen peroxide, and in another experiment to 0·5 per cent. 0·1 c.c. of water was admitted in the first case and 0·01 c.c. in the second. The water was vaporised by gentle heat, after which it was deposited as dew. In the first instance, the spectrum of nitrogen peroxide disappeared very quickly, and in the second it gradually faded away, only a trace of nitrogen peroxide being observed after an hour.

The presence of traces of liquid water therefore causes the absorption spectrum of nitrogen peroxide to vanish when it exists in low concentration.

(b) *Effect of Water Vapour on Nitrogen Peroxide.*—Since it was not possible to study the influence of very small quantities of water by the method just described, another apparatus was devised (Fig. 2), in which air, saturated with water vapour at different temperatures, was mixed with nitrogen dioxide, thus forming mixtures with varying proportions of water vapour according to the temperature of saturation of the air.

FIG. 2.



Apparatus for determining effect of water vapour on NO_2.

The current of air was obtained from a reservoir, and was measured by observing the number of bubbles per minute passing through a sulphuric acid drying apparatus. By means of a three-way cock the air could be sent either through the glass bulbs containing water to saturate it with aqueous vapour, or through a by-pass tube to the apparatus in which it was mixed with nitrogen dioxide. The nitrogen dioxide was generated in the large nitrometer from sodium nitrate in the presence of sulphuric acid and mercury, and from this was passed into the measuring tube. This consisted of a small, finely-graduated nitrometer with a T-piece fused on to one of the branches of the three-way cock at the top. One of the horizontal branches of the T was drawn out to a capillary, and the other was furnished with a stop-cock. The air was driven out from the branches of the T-piece by nitrogen dioxide from the large nitrometer, and then the graduated tube of the measuring apparatus was filled with the gas.

In order to obtain a regular and slow current of nitrogen dioxide the level of mercury in the compensating tube of the small nitrometer was gradually raised by allowing a very fine stream of mercury to flow into it from a capillary tube attached to a reservoir of mercury with an arrangement for keeping a constant head. The diameter of the compensating tube of the nitrometer was 3 cm., and the capillary allowed about 25 c.c. of mercury to drop per hour, and this delivered 2·1 cc. of nitrogen dioxide per hour.

The nitrogen dioxide was injected into the air stream by the capillary tube, and the mixture was then passed through a glass spiral in an oil bath heated to 130°, in order to realise the conditions of the experiments on nitrocellulose as far as possible. The gas, after leaving the spiral, was passed through the observation tube, and photographs were taken of the absorption spectrum of the nitrogen peroxide formed.

As a control experiment, the first photograph was taken of the spectrum of a mixture of nitrogen dioxide and dry air. The influence of different quantities of water vapour was then studied by varying the temperature at which the air was saturated.

In the last two experiments the air was saturated at 40° to obtain as great an effect as possible, but owing to the temperature of the surrounding air being 17·5° some of the water was deposited before the stream of moist air reached the nitrogen dioxide. The results are shown in the following table:

TABLE I.

Expt.	Rate of NO c.c. per hour.	Rate of air c.c. per hour. Dry.	Rate of air c.c. per hour. Wet.	Temp. of saturation.	Molecular proportion $H_2O:NO_2$.	Concentration calculated from NO used.	Concentration calculated from photos.
1	2·40	1028	—	Dry	—	0·0023	0·0017
2	1·80	1018	1045	11°	8·1	0·0017	0·0015
3	2·04	1018	1045	11	7·1	0·0020	0·0017
4	2·04	1018	1060	40	10·1	0·0019	0·0017
5	1·56	1018	1060	40	13·1	0·0015	0·0014

Another series with a slightly higher proportion of nitrogen dioxide gave similar results. These experiments show that at low concentrations nitrogen peroxide is not acted on by water in the form of vapour, and, consequently, the figures obtained in the study of the decomposition of nitrocellulose may be taken as representing the amount of nitrogen peroxide which is actually produced under the various conditions of experiment.

III. *Material Used for Experiments on Guncotton.*—The results given in this paper are, for the most part, obtained from stable guncottons. In each of the applications of the method to the decomposition of guncotton in the various ways to be described, a large number of experiments were performed, but for the sake of clearness and comparison the behaviour of two representative guncottons, called Guncotton No. 1 and Guncotton No. 2, will be described.

These guncottons were in the pulped condition and had a nitrogen content of 13 per cent. and a solubility in ether-alcohol of 10 per cent. That they are stable specimens of guncotton will be seen from the results of the following tests to which they were subjected:

TABLE II.

		Guncotton No. 1.	Guucotton No. 2.
Abel heat test at 76·6°		14′	18′
Will test at 135°	N per 2·5 grams guncotton in 4 hours	6·7 mg.	6·8 mg.
Fume test at 135°	Faint red fumes at	60 mins.	60 mins.
Bergmann and Junk's test	*Zeitsch. angew. Chem.*, 1905, 982, 1018, and 1074)—c.c. NO per 1 gram guncotton per 2 hours	1·30 c.c.	1·20 c.c.

The "trace" tests are those given by well-purified guncotton, and the tests made at a temperature involving a further decomposition also show that the materials are stable and disengage the minimum of nitrogen under the respective conditions of test.

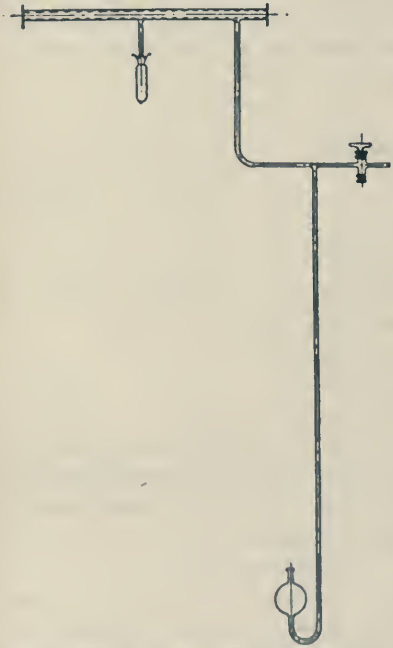
IV. *Application to Decomposition of Guncotton.*—

(a) *In a Vacuum.*—Several forms of apparatus were used in these experiments, the first pattern, which is shown in Fig. 3, consisting of—(1) A decomposition tube with mercury-sealed joint, the tube being kept at the desired temperature by immersion in an oil-bath of the Victor Meyer type kept at constant temperature; (2) an observation tube 40 cm. long, for the observation of the absorption spectrum of nitrogen peroxide, the source of light being an incandescent Welsbach mantle and the instrument a Hilger No. 1 table spectroscope with a single dense flint prism and fitted with a camera; (3) a Töpler vacuum pump; and (4) a manometer for registering pressure.

The second pattern is shown in Fig. 4. The apparatus differs in the following respects: (1) the decomposition tube is of greater volume, and the observation tube wider than in Fig. 3, and (2) an arrangement is made for filling the apparatus with carbon dioxide and for sweeping out the decomposition products of the guncotton by means of this gas. The decomposition products are then led over ignited copper asbestos and copper oxide asbestos, and the nitrogen is measured in a gas-burette over caustic potash which absorbs the excess of carbon dioxide.

The small diagram on the left-hand side of Fig. 4 shows a third pattern of decomposition tube from which the products of decomposition can be completely removed by a stream of carbon dioxide passing through a tube which reaches nearly to the bottom of the vessel.

Fig. 3.



Apparatus for observation of gases evolved in vacuo.

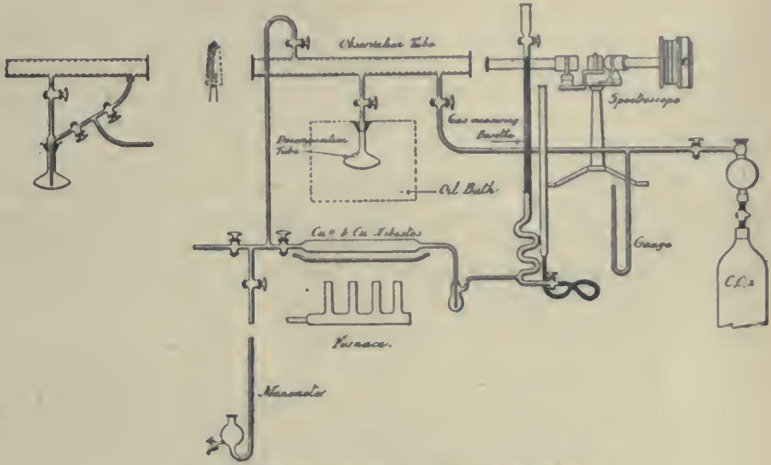
Glass cocks with mercury seals were used throughout the apparatus, which was exhausted until no bubble of gas was collected by the Töpler pump, and which was frequently tested for air by the introduction of nitrogen dioxide, when no trace of nitrogen peroxide could be detected by the spectroscope.

Process I.—Two grams of well-dried guncotton are introduced into the decomposition tube, which is then connected to the observation tube by means of a mercury joint, the apparatus is evacuated and the decomposition tube containing the guncotton is lowered into the bath at 135°. For half an hour the apparatus is kept connected to the pump and evacuated continuously to abstract water and air from the guncotton. The cock to the pump is then closed, and the fall in pressure is observed, whilst photographs of the absorption spectrum of the nitrogen peroxide evolved are taken at intervals.

Process II.—When the total nitrogen evolved is estimated in addition to the nitrogen as nitrogen peroxide, the procedure is as follows. The whole apparatus except the combustion tube is thoroughly evacuated, carbon dioxide is admitted, evacuated, and again admitted and evacuated; the guncotton is heated in the bath at 135° for ten minutes, carbon dioxide is admitted and passed through the whole apparatus, including the combustion tube, at a measured rate into an absorption burette. The apparatus, now quite free from air and filled with carbon dioxide, is shut off from the combustion tube and evacuated; the decomposition tube containing the guncotton being now surrounded by the bath at 135°, after half an hour of continuous evacuation the pump is shut off, and the actual experiment begins.

At intervals, the spectrum of nitrogen peroxide is observed, photographs are taken, and the fall in the level of the mercury in the manometer is noted every quarter of an hour during the course of the experiment, which is usually continued for four hours. At the end of the experiment the gaseous products of decomposition are swept out of the apparatus by a stream of carbon dioxide and led through the combustion tube, after which the gases, now consisting of carbon dioxide and nitrogen, pass into the absorption burette containing caustic potash, where the latter is measured, a small correction being made for the unabsorbed residue in the carbon dioxide used.

FIG. 4.



Apparatus for estimation of NO_2 *evolved in vacuo.*

The concentration of the nitrogen peroxide was obtained by direct comparison with the standard photographs described in the previous paper. The weight of nitrogen peroxide was then calculated from the concentration and the volume of the apparatus, and thus the weight of nitrogen existing as nitrogen peroxide was arrived at. The figures obtained in this way are compared in Table III with the total weight of nitrogen given by the combustion process just described:

Table III.

Decomposition of guncotton in a vacuum at 135°.

		Apparatus used.		Nitrogen evolved per 1 gram per 1 hour.		
Expt.	Gun-cotton.	Type.	Volume c.c.	as NO_2 mg.	total mg.	Ratio $\frac{N_2 \text{ as } NO_2}{\text{Total } N_2}$.
1	No. 1.	As in Fig. 3.	45	0·01	—	—
2	No. 2.	,,	61	0·05	—	—
3	No. 1.	As in Fig. 4. (But tube with deep decomp. tube of 3).	442	0·145	0·72	20 per cent.
4	No. 2.	,,	442	0·15	0·64	23 ,,
5	No. 1.	As in Fig. 4.	486	0·175	0·77	23 ,,
6	No. 2.	,,	486	0·21	0·85	24 ,,

In the early experiments in this series, of which Nos. 1 and 2 of Table III. are typical, the volume of the apparatus was small (Fig. 3), and the proportion of nitrogen peroxide observed was also small when reckoned on the guncotton present.

An examination showed that, although all moisture was carefully removed from the guncotton during its treatment immediately preceding the commencement of the experiment, water was gradually deposited during the experiment on the walls of the absorption tube and connexions. The effect of a trace of water in the liquid phase in removing nitrogen peroxide from a gaseous mixture has been dealt with above, and in consequence the volume of the apparatus was increased until the water-vapour proceeding from the normal decomposition of the guncotton was retained in the gaseous state, since it has been shown that no interaction takes place under these conditions.

The apparatus in Fig. 4 was devised for this purpose, and in this no deposition of moisture was ever observed during the four hours of experiment; the quantity of nitrogen as nitrogen peroxide was found to be largely increased, and in this series of experiments the total nitrogen with its relation to the nitrogen evolved as nitrogen peroxide was also determined.

Since by this modification in the volume of the apparatus a considerable increase in the quantity of nitrogen peroxide was obtained, numerous experiments were made with the object of obtaining the maximum proportion of nitrogen existing as nitrogen peroxide. Thus attempts were made to reduce the reaction of the nitrogen peroxide which went on to a very slight extent with the mercury of the manometer by introducing a fine capillary and a stopcock opened only at intervals above the level of the liquid; these resulted in only a trifling increase in the proportion. Another method employed for the same end was to use a decomposition tube in which the guncotton lay in a shallow layer (Fig. 4), thus permitting the free disengagement of nitrogen peroxide without passing through a layer of heated guncotton as in Fig. 3. The advantage gained was, however, only small.

Under the conditions of this experiment, that is, in a vacuum at 135°, guncotton disengages about 25 per cent. of the total nitrogen evolved in the form of nitrogen peroxide. The rest of the nitrogen is for the most part present as nitrogen dioxide.

(b) *Decomposition of Guncotton in a Stream of Carbon Dioxide* (*Will Test*).—This test (Will, "Untersuchungen über die Stabilität von Nitrocellulose," Erste und Zweite Mitteilungen) has been in constant use at Waltham Abbey for some considerable time and has been found to give satisfactory results in the case of ungelatinised nitrocellulose.

The method of working, which is that originally proposed by Will with a few modifications (Robertson, *J. Soc. Chem. Ind.*, 1902, **21**, 819), is as follows:

A stream of specially pure carbon dioxide from a cylinder of the liquefied gas is passed at the rate of 1 litre per hour (controlled by observing the number of bubbles per minute in a small gas washing bulb containing sulphuric acid) through 2½ grams of nitrocellulose in an oil-bath heated to 135°.

The current of carbon dioxide containing the gases produced by the decomposition of the nitrocellulose is passed through a copper combustion tube which is provided with two spirals of reduced copper gauze and layers of Kreusler's copper oxide, asbestos, and reduced copper asbestos. The oxides of nitrogen are by this means reduced to nitrogen and the organic gases oxidised to carbon dioxide. The gas is then passed into a measuring burette containing strong caustic potash solution, which absorbs the carbon dioxide and allows the volume of nitrogen to be read at intervals. A curve is plotted showing the weight of nitrogen evolved each quarter-hour, and the character and slope of the curve is a measure of the stability of the sample.

The general arrangement of the apparatus for estimation of the nitrogen peroxide disengaged under the conditions of the Will test is shown in Fig. 5.

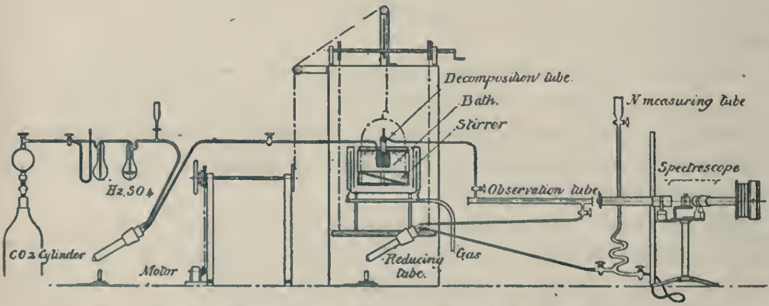
For the purpose of studying the amount of nitrogen peroxide given off by the guncotton, the gas after leaving the decomposition tube was passed through a tube which permitted its absorption spectrum to be photographed at intervals without interfering with the progress of the test.

In order to prevent the trace of oxygen due to air in the carbon dioxide from oxidising any of the nitrogen dioxide given off by the nitrocellulose, the gas was passed through a heated copper combustion tube containing Kreusler's reduced copper asbestos and copper gauze spirals to absorb any oxygen before it reached the decomposition tube. This was found to give the desired result, since on passing pure nitrogen dioxide into the current of carbon dioxide deoxidised in this way no traces of the absorption spectrum of nitrogen peroxide could be detected.

The tube through which the gas was passed for observing its spectrum was 40 cm. long with a side tube at each end, and the volume, which was 16 c.c., ensured the contents being changed about once every minute.

The gas, after passing through the observation tube, was led through a second copper tube, as in the ordinary Will test, so that the nitrogen present as peroxide and the total nitrogen evolved could be obtained from the same experiment and their ratio compared for different periods.

FIG. 5.



Apparatus for observing gases from Will test.

As a rule, a photograph was taken every quarter-hour at the same time as the volume of nitrogen was read, but in some duplicate experiments one every half-hour was considered sufficient.

The plates from each experiment were developed together in the same dish to ensure uniformity. The negatives were then compared with the standard and the amount of nitrogen present as peroxide calculated.

This was done in a manner similar to that already described (p. 771), and for comparison with the usual results of the Will test in which the quantity of nitrogen is expressed in milligrams per quarter-hour disengaged from 2·5 grams of guncotton at 135°, the nitrogen existing as peroxide was also calculated for the same period (during which 250 c.c. of carbon dioxide passed through the guncotton), c being the percentage concentration of nitrogen peroxide in the carbon dioxide by volume and 27° the temperature of preparation of the standard

Fig. 2.

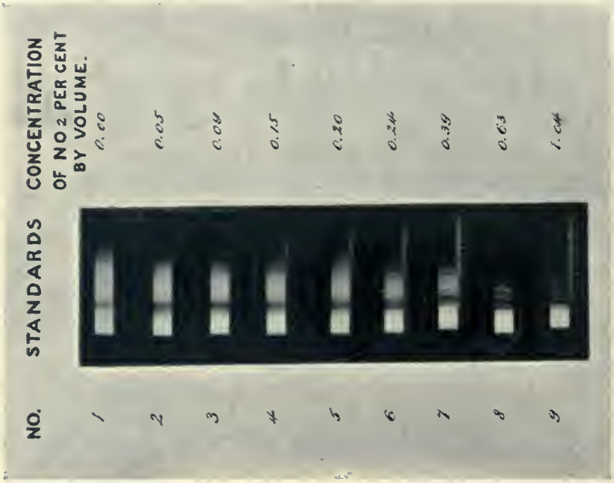
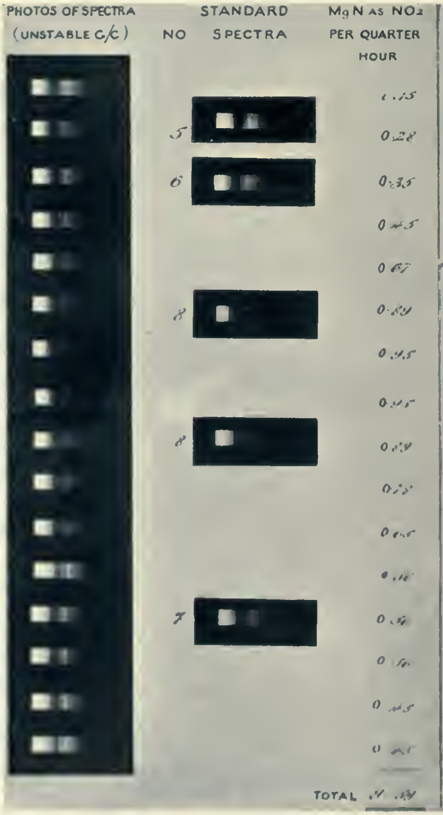
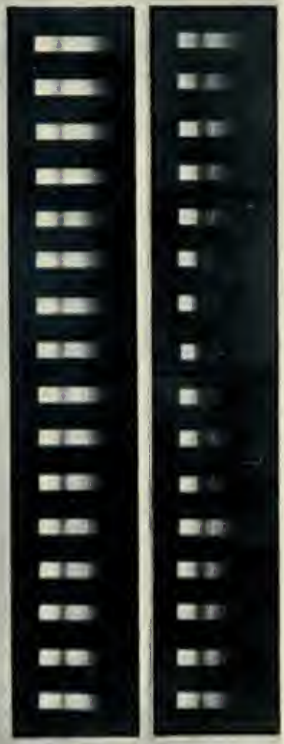


Fig. 6.


PHOTOS OF SPECTRA (UNSTABLE G/C)
NO
STANDARD SPECTRA
Mg N AS NO2 PER QUARTER HOUR
5
6
8
8
7
0.28
0.35
0.45
0.67
0.89
0.95
0.95
0.89
TOTAL

Will test.

Fig. 7.



Stable G.C. Unstable G.C.
NO$_2$ *in Will test.*

[*To face p. 775.*

negatives, thus, $c \times 0{\cdot}627 \times \frac{273}{300} \times 250 = c \times 1{\cdot}43$, a useful factor for expressing concentration of nitrogen peroxide in terms of milligrams of nitrogen existing as nitrogen peroxide per quarter-hour.

The comparisons of spectra with the standard spectra were made with the original negatives, but for the purpose of demonstrating the method the prints are here reproduced, and, although much detail is lost in the reproduction, the method of matching the standard photograph against the experimental result is shown in Fig. 6.

Examples are given in Fig. 7 of the difference in appearance presented by the spectra from two guncottons, the one stable and the other unstable, the photographs being taken under the same conditions every quarter hour.

The results obtained by this method in the case of the two samples of stable guncotton used in the vacuum experiments are given in the following table :

TABLE IV.

Decomposition of guncotton in Will test at 135°.

	Guncotton No. 1.		Guncotton No. 2.	
Quarter hours.	Nitrogen as NO_2. mg.	Nitrogen total mg.	Nitrogen as NO_2. mg.	Nitrogen total mg.
1	0·05	0·13	0·02	0·19
2	0·10	0·24	0·05	0·30
3	0·14	0·35	0·07	0·41
4	0·17	0·38	0·08	0·41
5	0·18	0·46	0·14	0·41
6	0·19	0·46	0·21	0·41
7	0·19	0·46	0·21	0·50
8	0·20	0·46	0·21	0·45
9	0·20	0·52	0·21	0·45
10	0·20	0·52	0·21	0·50
11	0·20	0·46	0·20	0·41
12	0·20	0·46	0·20	0·45
13	0·20	0·46	0·20	0·45
14	0·19	0·42	0·20	0·50
15	0·20	0·46	0·20	0·50
16	0·20	0·46	0·20	0·47
	2·81	6·70	2·61	6·80
Ratio, $\frac{N_2 \text{ as } NO_2}{\text{Total } N_2}$.	42 per cent.		39 per cent.	

As the magnitude of the ratio of nitrogen as peroxide to the total nitrogen evolved in the Will test was so remarkable, the possibility of checking the figures obtained by the spectroscopic method was considered. The method employed was an analytical one and was as follows.

The gases after leaving the decomposition tube were led through two small absorption tubes containing strong sulphuric acid, and then into the usual caustic potash absorption burette without the interposition of a heated combustion tube.

After the usual four hours the sulphuric acid was shaken up in a nitrometer with mercury; the gases unabsorbed by the potash solution were also examined for nitrogen dioxide by absorption with Divers' reagent (Trans., 1899, 75, 82), and for nitrogen by taking the difference between the total unabsorbed gas and the carbon monoxide found. A correction was made for the small quantity of nitrogen from the carbon dioxide. If, as claimed by Will, nitrogen dioxide were the chief constituent of the nitrogenous gases, it would pass the sulphuric acid bulbs unabsorbed, and be collected over the potash solution with a volume twice that of the nitrogen found when the gases are led through a combustion tube. Instead of this, there was a large absorption of nitrogenous gases by the sulphuric acid, and a small volume of nitrogen dioxide was collected over the caustic potash. The details are given below, and it will be observed that they confirm the spectroscopic results.

It has been shown (Lunge, "Sulphuric Acid and Alkali," 3rd ed., p. 214) that when a mixture of nitrogen dioxide and peroxide is passed into sulphuric acid the mixture reacts as trioxide, forming the fairly stable compound $OH\cdot SO_2\cdot NO_2$. Half of the nitrogen dioxide obtained in the nitrometer from the sulphuric acid is therefore to be reckoned as dioxide and half as peroxide:

TABLE V.

	Guncotton No. 1.		
	I.	II.	III.
N as NO_2, half nitrometer result	2·5	2·5	2·6
N as NO, half nitrometer result + unabsorbed by KOH	2·5	2·5	2·6
N as N_2	1·7	1·0	0·9
N Total	6·7	6·0	6·1
N as NO_2 (spectroscopic)	—	2·8	—
N Total (Will test)	—	6·7	—

These results are entirely confirmatory of those obtained by the spectroscopic method. Thus, of the total nitrogen evolved in the ordinary Will test (6·7 mg. N), the nitrogen existing as peroxide is found by absorption in sulphuric acid to be 2·5 to 2·6 mg. or 37 to 39 per cent. as against 2·8 mg. or 42 per cent. found by the spectroscopic method.

The presence of nitrogen peroxide in the gases of the Will test was indicated also by the small volume of gas obtained when the heated combustion tube was cut out of the usual system. When this was done the nitrogen peroxide and some of the dioxide were absorbed by the potash solution, only a relatively small quantity of the dioxide remaining unabsorbed.

When it was found that nitrogen peroxide was a large constituent of the nitrogenous gases evolved when guncotton is decomposed with continuous removal of the volatile products of decomposition, experiments were made to ascertain how far this result was dependent on the conditions of experiment.

Influence of Rate of Carbon Dioxide.—When guncotton is allowed to decompose in a steady atmosphere of carbon dioxide (see p. 779) it is found that much less nitrogen peroxide is obtained among the decomposition products than when these are continuously removed as in the Will test.

The most probable explanation is that whilst the nitrogen peroxide in the latter case is removed in the stream of carbon dioxide, in the former it is kept in contact with the guncotton throughout the experiment and undergoes reduction either by the nitrocellulose or organic impurities present.

It follows from this that if the rate of the stream of carbon dioxide were gradually reduced, the proportion of nitrogen peroxide evolved should decrease until it reached the figure obtained from the decomposition in an unchanged atmosphere of the same gas.

To see whether this was the case the following experiments were made in which the rate of the current of gas in the Will apparatus was very much reduced.

TABLE VI.

Carbon Dioxide.

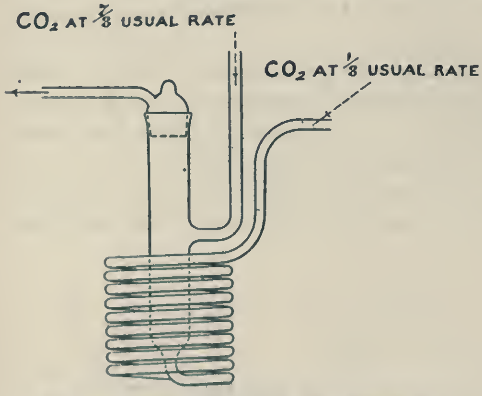
Influence of reduced rate of CO_2 *in Will test at* 135°.

Expt.	Gun-cotton used.	Rate of carbon dioxide.		Per cent. of N_2 existing as NO_2.	
		Passing through guncotton.	Entering above guncotton.		
1	No. 1	1/3 of normal	—	36	No moisture deposited in tubes
2	No. 1	1/4 of normal;	—	35	No moisture deposited in tubes
		then at normal.	—	48	No moisture deposited in tubes
3	No. 1	Normal; then at	—	40	No moisture deposited in tubes
		1/8 of normal	—	[9·0]	Moisture deposited.
4	No. 1	1/8 of normal	7/8 of normal	18·0	No moisture deposited in tubes.
5	No. 1	1/10 of normal	9/10 of normal	20·0	No moisture deposited in tubes.

It will be seen that by reducing the rate from the normal one of 1,000 c.c. carbon dioxide per hour to a quarter of its former value, only a comparatively small alteration is effected in the relation between the nitrogen existing as peroxide to the total nitrogen evolved. On reducing the rate still further to an eighth, a very marked diminution occurs (Expt. 3); but as moisture was observed in the tubes and as this is a condition favourable to the absorption of nitrogen peroxide (see p. 768), it became necessary to ensure that the vapour tension of the water produced by the decomposition was kept sufficiently low to prevent deposition of liquid water. This was done by fusing a side tube on to the decomposition tube so that a diluent stream of carbon dioxide was introduced immediately above the guncotton, as is shown in Fig. 8.

This stream of carbon dioxide was kept at seven-eighths of the normal rate while that passing through the guncotton was reduced to one-eighth of the normal. In this way the total volume of gas passing through the guncotton was small, and water vapour formed by the decomposition was at once diluted and thus prevented from being deposited as liquid in the cooler parts of the tube. The result of this treatment was to reduce the proportion of nitrogen existing as peroxide to 18 per cent., a figure only slightly higher than that found when guncotton is heated in a steady atmosphere of carbon dioxide (p. 779). This experiment shows that the effect of the constant stream of carbon dioxide through the guncotton, under the conditions of the Will test, is to carry away the nitrogen peroxide normally formed during the decomposition of the nitrocellulose molecule, and it exemplifies the action of water on the one hand, and of contact with heated guncotton on the other, in reducing the concentration of nitrogen peroxide.

FIG. 8.



Will decomposition tube for rate experiments.

The results given above for the guncottons Nos. 1 and 2 are typical of a large number of guncottons which have been examined. These guncottons—of widely different origin and of good stability as established by the Will and other tests—all decomposed in the same manner, giving a high proportion of nitrogen peroxide.

The percentage of nitrogen as peroxide in the gases evolved remains high when the guncotton has been previously purified by methods additional to the usual boiling process. This was demonstrated with guncottons repeatedly extracted with ether and with alcohol and also with a sample reprecipitated from acetone solution by water.

An experiment was made to determine the course of the decomposition when the guncotton was heated for a much longer period than the usual four hours of the Will test. The results of this experiment are given in Table VII, in which will be found the total nitrogen and that evolved as nitrogen peroxide together with the loss of nitrogen calculated on the original guncotton of 13 per cent. of nitrogen. It will be seen that for a period five times longer than the usual Will test the proportion of nitrogen existing as peroxide to total nitrogen in the gases evolved is more than 40 per cent.:

TABLE VII.

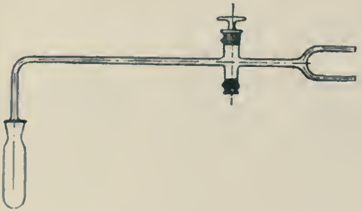
Quarter hours.	Average N_2 per $\frac{1}{4}$ hour.	Average N_2 as NO_2 per $\frac{1}{4}$ hour.	Ratio per cent. $\frac{N_2 \text{ as } NO_2}{N_2 \text{ Total.}}$	Loss in nitrogen content of guncotton per cent.
9—16	0·44 mg.	0·24 mg.	54	0·28
17—32	0·44 ,,	0·24 ,,	54	0·56
33—48	0·45 ,,	0·24 ,,	53	0·87
49—64	0·40 ,,	0·21 ,,	52	1·12
65—80	0·44 ,,	0·20 ,,	45	1·40
81—96	0·43 ,,	0·13 ,,	30	1·67
97—112	0·41 ,,	0·13 ,,	32	1·93
113—128	0·43 ,,	0·14 ,,	32	2·20
129—144	0·44 ,,	0·13 ,,	30	2·48
145—160	0·47 ,,	0·13 ,,	28	2·78
161—176	0·44 ,,	0·11 ,,	25	3·06
177—192	0·49 ,,	0·10 ,,	20	3·37
193—208	0·46 ,,	0·09 ,,	19	3·64
209—224	0·49 ,,	0·05 ,,	10	3·97
225—240	0·49 ,,	0·04 ,,	8	4·29

(c) *Decomposition of Guncotton in an Unchanged Atmosphere of Carbon Dioxide.*—The decomposition in a constantly changing atmosphere of carbon dioxide has been described in the last section; in this, some experiments will be described in which the guncotton was decomposed in an unchanged atmosphere of carbon dioxide at ordinary pressure.

In the first series of experiments (Fig. 9) a small decomposition tube was used, and this was connected, on the one hand, to an observation tube, and on the other to the pump and a cylinder of carbon dioxide. Every precaution was taken to prevent air being introduced into the apparatus, the guncotton was well dried and finally heated in the bath at 135° in an atmosphere of carbon dioxide which was changed both before and during this preliminary heating; carbon dioxide was finally admitted, and after five minutes the stopcock was momentarily opened to relieve excess of pressure. After each period of the experiment the gases formed in the decomposition tube were allowed to expand into the observation tube, which, together with all connecting tubes, had been filled with carbon dioxide and exhausted. Before starting on another period the residual gases were pumped out of the decomposition tube, which was then filled with carbon dioxide as before. The absorption spectrum of the nitrogen peroxide was photographed and the concentration estimated in the manner already described. From this the quantity of peroxide present in the gases was calculated as before.

In the second series of experiments (Fig. 4) both the nitrogen existing as peroxide and the total nitrogen evolved during the experiment were estimated. The method of carrying out the experiment was exactly as described in the vacuum series of experiments, up to and including the thirty minutes' evacuation in a vacuum at 135° to eliminate all air and moisture. Carbon dioxide was then admitted until it was at atmospheric pressure in the decomposition vessel, after which the experiment was started.

Fig. 9.



After each hour the gaseous contents of the decomposition tube were drawn into the evacuated observation tube and the concentration of the nitrogen peroxide observed. At the completion of the fourth hour all the gases were swept out of the apparatus by a stream of carbon dioxide, passing over heated copper and copper oxide, and the total nitrogen obtained as in the vacuum experiments.

The results of the experiments with the same two stable guncottons as were used in the previous experiments are given in Table VIII:

Table VIII.

			Apparatus used.			Mg. nitrogen evolved per 1 gram guncotton (average of 4 separate hours).		
Expt. No.	Series.	Gun-cotton.	Type.	Volume of decomposition tube in c.c.	Volume of observation tube in c.c.	As NO_2.	Total.	Percentage ratio $\frac{N \text{ as } NO_2}{N \text{ (Total)}}$.
1	First	No. 1	As in Fig. 10	17	420	0·07	—	—
2	,,	No. 2	,,	17	420	0·06	—	—
3	Second	No. 1	As in Fig. 4	55	495	0·11	—	—
4	,,	No. 1	,,	55	495	0·11	0·88	13
5	,,	No. 2	,,	55	495	0·12	—	—
6	,,	No. 2	,,	55	495	0·12	0·82	15

It will be seen that only a small quantity of nitrogen peroxide was obtained from the small decomposition vessel. A slight mist was observed to condense in the capillary tube between the decomposition vessel and the observation tube, on opening the cock admitting the products of decomposition into the latter, and the presence of this moisture was assumed to be the cause of the reduction of the peroxide to this small quantity.

In the second series no moisture was observed in the apparatus and more peroxide was obtained. The apparatus being adapted for the estimation of the total nitrogen, this was obtained for the purpose of arriving at the ratio of nitrogen existing as peroxide to total nitrogen under the conditions of this experiment. The table shows this to be from 13 to 15 per cent., or less than in the case of the vacuum experiments and very much less than in the case of the ordinary Will test. The decreased ratio is doubtless due to the reduction of the nitrogen peroxide by contact with the heated guncotton, a condition which occurs to a much greater extent in this experiment than in any of those yet described, since the gases are not removed from the decomposition vessel until after the expiration of one hour.

(d) *Decomposition of Guncotton in Presence of Nitrogen Dioxide.*—The effect of nitrogen dioxide on the decomposition was studied in three different ways.

(1) In a stream of the gas under the conditions of the Will test at 135°, the apparatus used being similar to that in Fig. 5.

The cylinder of carbon dioxide was replaced by a reservoir of nitrogen dioxide, and the amount passed was measured by the difference in level of the potash solution in the reservoir. The gas was tested spectroscopically and found to be free from nitrogen peroxide.

In this experiment the combustion tube and gas-measuring burette were omitted, the only measurement taken being that of the concentration of nitrogen peroxide.

(2) In an unchanged atmosphere of nitrogen dioxide at 130°, using a small decomposition tube of the type shown in Fig. 10.

(3) In an unchanged atmosphere of nitrogen dioxide at 130°, using the larger decomposition vessel of Fig. 4.

The method of experiment in (2) and (3) was similar to that used in studying the decomposition in carbon dioxide, and the results are given in Table IX :

TABLE IX.

				Apparatus used.			Nitrogen as NO_2 per hour in mg.					
Expt. No.	Series.	Temp.	Gun-cotton.	Type.	Volume of decomposition tube in c.c.	Volume of observation tube in c.c.	1st hour.	2nd hour.	3rd hour.	4th hour.	5th hour.	6th hour.
1	First	135°	No. 1	As in Will test	—	—	0·34	0·45	0·49	0·51	0·49	0·48
2	Second	130°	No. 1	As in Fig. 10	17	100	0·18	0·19	0·17	0·21	—	—
3	,,	130°	No. 1	,,	17	100	0·19	0·16	0·07	0·06	—	—
4	Third	130°	No. 1	As in Fig. 4	55	495	0·63	0·47	0·63	0·39	—	—

It appears from the above table that the quantity of nitrogen peroxide evolved under the conditions just described is considerably greater than that obtained when an atmosphere of carbon dioxide is used, which suggests that the oxides of nitrogen cause an acceleration of the rate of decomposition.

(e) *Decomposition of Guncotton in Air.*—In the foregoing experiments the action of the oxygen of the air has been carefully eliminated with the object of ascertaining the actual method of decomposition of guncotton; in the experiments described in this section the guncotton was permitted to decompose in air under such conditions that the nitrogen evolved as dioxide and peroxide was observed and estimated as peroxide.

The following table contains the results of some of these experiments:

TABLE X.

				Volume.			
Expt. No.	Series.	Gun-cotton used.	Apparatus used.	Decomposition tube in c.c.	Observation tube in c.c.	Temp. of Expt.	Nitrogen evolved per 1 gram guncotton per hour in mg.
1	First	No. 1	Fig. 5, air stream; no reduction tube nor burette	—	—	135°	0·54
2	,,	No. 2	,, ,,	—	—	135	0·62
3	Second	No. 1	Air.—First hour	11	93	130	0·05
4	,,	No. 2	,, ,,	11	93	,,	0·06
5	,,	No. 1	,, ,,	17	93	,,	0·09
6	,,	No. 2	,, ,,	17	93	,,	0·04
7	,,	No. 1	,, ,,	33	93	,,	0·17
8	,,	No. 2	,, ,,	,,	93	,,	0·18
9	,,	No. 1	,, Fourth hour	,,	420	,,	0·29
10	,,	No. 2	,, ,,	,,	,,	,,	0·31
11	,,	No. 1	,, 26th hour	,,	,,	,,	0·29
12	,,	No. 2	,, ,,	,,	,,	,,	0·34

It will be seen from this table that the nitrogen evolved in a stream of air from guncotton heated to 135° approached the figure found when it was decomposed in a stream of carbon dioxide. The influence of the small size of the decomposition vessel was also brought out in this series of experiments, much higher results being obtained when the possibility of deposition of water was lessened (Expts. 7 and 8). Two experiments were carried on for twenty-six hours, pumping out the products every hour, when it was found that the evolution of nitrogen remained practically constant during this period. If the traces of nitrogen peroxide remaining from a previous hour were permitted to remain in the tube, a large increase in the decomposition was obtained. Observing this precaution, the nitrogen evolved at 130°, was found to be 0·3 mg. per gram of guncotton per hour; if the effect of increase in temperature is similar to that observed by Will, namely, double the evolution for a rise of 5°, the

SUMMARY AND DISCUSSION OF RESULTS.

TABLE XI.—*Collected Results of Decomposition of Guncotton.*

Experiment. Table.	No.	Gun-cotton used.	Fig.	Apparatus used, and method.	Temp.	Volume of decomposition tube in c.c.	Volume of observation tube in c.c.	Nitrogen evolved per 1 gram guncotton per hour in mg. as NO_2.	Total.	Percentage ratio $\frac{N_2 \text{ as } NO_2}{N_2 \text{(total)}}$.
IV.	1	No. 1	5	CO_2 stream ; Will test	135°	—	—	0·28	0·67	42
	2	No. 2	5		135	—	—	0·26	0·68	39
VI.	3	No. 1	5	CO_2 stream ; slow rate ; moisture deposited	135	—	—	0·06	—	9
	4	No. 1	5 & 8	CO_2 stream ; slow rate ; no moisture deposited	135	—	—	0·16	0·81	20
III.	3	No. 1	3 & 4	Vacuum ; decomposition and observation tubes connected	135	12	430	0·145	0·72	20
	4	No. 2	3 & 4		135	12	430	0·15	0·64	23
	5	No. 1	4		135	43	453	0·175	0·77	23
	6	No. 2	4		135	43	453	0·21	0·85	24
	1	No. 1	3	Vacuum ; decomposition and observation tubes connected ; small app. ; moisture deposited	135	12	33	0·01	—	—
	2	No. 2	3		135	17	44	0·05	—	—
VIII.	4	No. 1	4	CO_2 atmosphere ; decomposition and observation tubes not connected	135	55	495	0·11	0·88	13
	5	No. 2	4		135	55	495	0·12	0·82	15
	1	No. 1	10	CO_2 atmosphere ; decomposition and observation tubes not connected ; moisture deposited	135	17	420	0·07	—	—
	2	No. 2	10		135	17	420	0·06	—	—
IX.	1	No. 1	5	NO stream	135	—	—	0·42	—	—
	2	No. 1	10	NO atmosphere ; small apparatus	130	17	100	0·14	—	—
	4	No. 1	4	NO atmosphere ; large apparatus	130	55	495	0·53	—	—

result is very similar to the quantity of nitrogen disengaged under the conditions of the Will test.

It is evident from Table XI that the conditions under which guncotton decomposes exercise an influence on the nature and quantity of the gaseous nitrogenous products, and it is necessary to eliminate the effects of disturbing conditions before arriving at the actual chemical reactions taking place. The first cause tending to decrease the proportion of nitrogen peroxide is the presence of liquid water produced by the decomposition of the guncotton, and in all cases where this occurs the effect is the same, namely, a more or less complete removal of the nitrogen peroxide owing to its having reacted with the water to form nitrous and nitric acids. This was observed in the small vacuum apparatus, in the decomposition in an unchanged atmosphere of carbon dioxide, and in the Will test if the current of carbon dioxide was very slow.

The second cause effecting the composition of the gases is action between the nitrogen peroxide originally evolved and the heated guncotton or its decomposition products. This appears to have a considerable effect, since under the conditions of the Will test, when the gases are continuously removed, the proportion of nitrogen peroxide to total nitrogen is greater than in any other method, and when the rate of removal is reduced it falls from 40 to 20 per cent.

In a vacuum, although the gases are removed with perhaps greater ease than in the Will test, they are free to diffuse back and react with the heated guncotton during the whole period of the experiment.

The effect is also shown in the experiments on decomposing guncotton in an unchanged atmosphere of carbon dioxide; here the nitrogen peroxide during the hour for which the heating was continued was in contact with the heated guncotton, with the result that the proportion of nitrogen peroxide fell to 13—15 per cent., which is one-third of that obtained when the gases were continuously removed. This loss may be due to absorption of the gas as such, or to its reduction to nitrogen dioxide. In the first case, the total amount of nitrogenous gases evolved would be reduced, but it is not possible to draw any deductions from the total quantity of nitrogen evolved, since in all cases in which the nitrogen peroxide is low owing to prolonged contact with the guncotton there may be a compensating increase in the total decomposition caused by the action of the gases on the guncotton. The experiments in an atmosphere of nitrogen dioxide point to an action of this kind, and the following extract from Table XI shows that there is a slight but decided increase in total nitrogen when the proportion of nitrogen peroxide is low:

No.	Decomposition.	Percentage ratio $\frac{N_2 \text{ as } NO_2}{\text{Total } N_2}$.		Total N_2 in mg.	
IV. 1	Will test......................	42		0·67	
III. 3	In vacuum..................	20	21·5	0·72	0·75
III. 5	,, ...	23		0·77	
VII. 4	In atmosphere of CO_2 ..	13		0·88	

The Will test is the method of decomposition which seems to be most free from complications caused by the by-products, and consequently the results given by it represent as nearly as can be obtained at present the course of the inherent decomposition of guncotton. By its means the actual or intrinsic stability of two samples may be compared, although it is not necessarily the best adapted for a practical stability test, since under ordinary conditions of storage the by-products are retained in close contact with the explosive. The presence of solid catalysts has long been considered to exercise an influence on the decomposition, and the results obtained in the present paper indicate that the gaseous products also have a measurable effect.

The presence of 40 per cent. of the total nitrogen in the form of peroxide is opposed to the results of the previous workers on this subject, but this disagreement is most probably due to their use of unsuitable apparatus and less perfect methods of estimating this gas.

Will concludes that practically the whole of the nitrogen is given off in the form of nitrogen dioxide, and gives the equation $C_{12}H_{15}(NO_2)_5O_{10} = C_{10}H_3O_8N + 4NO + 6H_2O + 2CO$ for the decomposition. This is based on the analysis of a product remaining after long-continued heating and the ratio of water (found by absorbing in a calcium chloride tube) to nitrogen in the gas evolved.

In confirmation, he quotes the observation that when the combustion tube is not sufficiently hot twice the usual volume of gas is obtained.

From Will's paper it appears that the analytical figures obtained by him do not agree with the calculated formula, $C_{10}H_3O_8N$:

Found ; $C = 44·4$; $H = 2·4$; $O = 47·9$; $N = 5·3$.
$C_{10}H_3O_8N$ requires $C = 45·3$; $H = 1·1$; $O = 48·3$; $N = 5·3$ per cent.

so that the equation is of very slight value. Moreover, the observation that the volume of gas is doubled if the combustion tube is not properly heated does not differentiate between nitrogen dioxide and peroxide, since the latter gas in these circumstances would be reduced to dioxide, the final result being the same, whatever the proportions of the two gases.

It has been previously mentioned in this paper that the volume of gas obtained when the combustion tube is omitted is less than the usual volume of nitrogen, which conclusively shows that nitrogen peroxide is present, the loss being due to absorption of dioxide and peroxide in the potash solution.

The experiment of long duration, quoted on p. 779, was carried out in a similar manner to that described by Will, and, for the period during which it was continued, confirms his result that the total quantity of nitrogen evolved per quarter hour remains constant. This was not the case with the composition of the gases, since the ratio of nitrogen as peroxide to total nitrogen, which remained at 40 to 50 per cent. for the first eighty quarter-hours (five times the period of the usual test), fell to about 10 per cent. after 260 quarter-hours, when the guncotton, originally containing 13 per cent. of nitrogen, had lost nitrogen equal to 4 per cent.

It is therefore evident that the equation proposed by Will does not represent the primary mode of decomposition of guncotton, as no account is taken of the presence of nitrogen peroxide; nor do his equation and formula agree with his analytical figures, while his observation of the double volume of gas is equally in agreement with the presence of nitrogen peroxide.

The long-continued experiments also serve to throw some further light on the results obtained by Hoitsema and Saposchnikoff, since it appears that the products of continued heating give a smaller proportion of nitrogen peroxide than is obtained by the action of heat on a pure nitrocellulose. But in the early stages of decomposition, and while the substance can still be described as a "nitrocellulose," the nitrogen is to a large extent evolved as peroxide.

The results of this research may be briefly summarised in the statement that, although previous observers have stated that only traces of nitrogen peroxide exist in the gaseous decomposition products of guncotton, it has been shown that, when due precautions are taken to exclude the action of liquid water and of the heated guncotton on the gases evolved, nearly one-half of the nitrogen evolved is present as peroxide, even when a considerable proportion of its nitrogen has already been disengaged from the guncotton molecule.

Finally, we would like to express our indebtedness to Lt.-Col. Sir Frederic Nathan for his valuable assistance and advice in connexion with this and the preceding paper.

ROYAL GUNPOWDER FACTORY,
WALTHAM ABBEY.

LXXII.—*An Isomeric Change of Dehydracetic Acid.*

By John Norman Collie and Thomas Percy Hilditch.

Recently it was noticed during the preparation of a large quantity of triacetic lactone, that if sulphuric acid of about 85 instead of 90 per cent. strength was used, the yield of triacetic lactone was considerably reduced. The triacetic lactone is prepared by heating dehydracetic acid with sulphuric acid of about 90 per cent. for a short time to 135° (Collie, Trans., 1891, **59**, 607). The product is then poured into water and the triacetic lactone crystallises out. When 85 per cent. sulphuric acid is used only a small quantity of the lactone separates when the product of the reaction is poured into water, but a further crop of crystals can be obtained by nearly neutralising the acid solution with solid sodium carbonate. At first these were thought to be impure triacetic lactone, but after purification by several recrystallisations they were found to have a melting point 99°, whilst the lactone melts at 189°.

The crystals were acid to litmus paper, and more soluble in water than triacetic lactone.

On analysis, the mean of three concordant results was:

$C = 56{\cdot}8$. $H = 4{\cdot}9$;

$(C_2H_2O)_n$ requires $C = 57{\cdot}1$; $H = 4{\cdot}8$ per cent.

On titration with soda the mean of several experiments gave the equivalent of the acid as 165. This is too high for triacetic lactone, $C_6H_6O_3 = 126$, but it agrees well with $C_8H_8O_4 = 168$.

The molecular weight was determined by the boiling point method, the molecular weight of 169 was obtained as the mean of three experiments.

From these results the compound is obviously isomeric with dehydracetic acid.

When boiled with hydrochloric acid it is decomposed into dimethylpyrone and carbon dioxide. From 1 gram of the acid 0·75 gram of dimethylpyrone was obtained. The dimethylpyrone was identified by its melting point, 132°, its yellow barium salt, and the production of diacetylacetone, which gives a blood-red coloration with ferric chloride,

$$C_8H_8O_4 = C_7H_8O_2 + CO_2.$$

By heating the compound to about 200°, it decomposed in an exactly similar manner, an almost quantitative yield of carbon dioxide and dimethylpyrone being produced. When boiled with excess of strong baryta solution it gave no yellow compound, but after a short time a barium salt crystallising in needles separated from the hot solution; these were filtered off, and in the filtrate, which had a strong odour of acetone, an acetate was found.

The barium salt on analysis gave Ba = 53·9; this agrees with the percentage of barium in barium malonate:

$C_3H_2O_4Ba,H_2O$ requires Ba = 53·3 per cent.

That the salt was barium malonate was proved by the fact that the free acid from the barium salt on heating gave carbon dioxide and acetic acid.

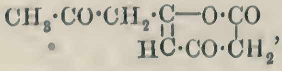
The electrical conductivity of the acid was found to be K = 0·00152.

The acid seems, therefore, to be in most respects identical with an acid obtained by Feist (*Annalen*, 1890, **257**, 253) by the action of sulphuric acid on the dichloride of dehydracetic acid. The chief difference was in the electrical conductivity, which Feist found to be K = 0·0385.

Several salts of the acid were prepared from a solution of the sodium salt. Silver nitrate gives a white precipitate soluble in hot water; mercuric chloride, a white precipitate; mercurous nitrate, a grey precipitate, which decomposes on warming and evolves carbon dioxide; ferric chloride, a dark yellow coloration and a slight precipitate on boiling: this, however, may be due to the decomposition of the sodium salt, for it was found that on boiling the sodium salt the solution became distinctly alkaline, and when acid was added, dehydracetic acid was precipitated. The dehydracetic acid melted at 108°, and when viewed under the microscope it was identical with the ordinary acid. Considerable decomposition, however, took place, as well as the change of the acid back to dehydracetic acid, for when a solution of the sodium salt was evaporated to half its bulk the distillate was found to contain acetylacetone, which gave a deep blood-red coloration with ferric chloride.

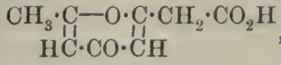
The free acid when heated in a sealed tube with strong ammonia gave an ammonium salt of a lutidonecarboxylic acid; the free acid melted at 258° and was the same as an acid obtained from ethyl β-aminocrotonate by heat (Collie, *Annalen*, 1884, **226**, 297). When heated, it decomposed quantitatively into 2 : 6-dimethylpyridone.

This interesting isomeric change of dehydracetic acid, when heated with sulphuric acid, to a pyronecarboxylic acid, and the reverse change when heated with soda may be expressed as follows:



$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot C{-}O\cdot CO \\ \qquad\qquad\quad\ \ \| \qquad\quad | \\ \qquad\qquad\quad HC\cdot CO\cdot CH_2 \end{array}$$, dehydracetic acid.

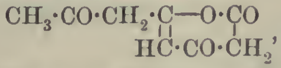
$CH_3\cdot C(OH){:}CH\cdot CO\cdot CH{:}C(OH)\cdot CH_2\cdot CO_2H$, intermediate compound in acid solution.



$$\begin{array}{l} CH_3\cdot C{-}O\cdot C\cdot CH_2\cdot CO_2H \\ \quad HC\cdot CO\cdot CH \end{array}$$

, 2-methylpyrone-6-acetic acid.

$CH_3\cdot CO\cdot CH_2\cdot C(OH)\colon CH\cdot CO\cdot CH_2\cdot CO_2Na$, intermediate compound in alkaline solution.



$$\begin{array}{l} CH_3\cdot CO\cdot CH_2\cdot C{-}O\cdot CO \\ \qquad\qquad\quad HC\cdot CO\cdot CH_2 \end{array}$$

, dehydracetic acid.

The above formula easily explains the formation of a lutidonecarboxylic acid and also the formation of malonic acid, acetone, and acetic acid when the acid is heated respectively with ammonia or with concentrated baryta solution.

THE ORGANIC LABORATORY,
UNIVERSITY COLLEGE, LONDON.

LXXIII.—*Measurements of the Velocities of Saponification of the* l-*Menthyl and* l-*Bornyl Esters of the Stereoisomeric Mandelic Acids.*

By ALEX. MCKENZIE and HERBERT BRYAN THOMPSON, M.Sc.

THE esters, *l*-bornyl *d*-mandelate and *l*-bornyl *l*-mandelate, are diastereoisomeric and not enantiomorphous. They can accordingly undergo saponification by alkali with different velocities, and the method of Marckwald and McKenzie for resolving inactive compounds into their optically active components has been applied in the case of *r*-mandelic acid by completely esterifying it with *l*-borneol and then submitting the resulting *l*-bornyl *dl*-mandelate to fractional saponification with alcoholic potassium hydroxide (Trans., 1904, **85**, 378). The alcoholic solution of the latter ester may be regarded as containing equal amounts of the diastereoisomerides and it formed, when heated with an amount of potassium hydroxide insufficient for complete saponification, potassium mandelate, the aqueous solution of which was carefully freed from borneol and residual bornyl esters and on polarimetric examination was lævorotatory.

On first considerations this result indicated that *l*-bornyl *l*-mandelate undergoes saponification more quickly than does the isomeric *d*-mandelate, a view, however, which, in the first instance, was not in accordance with what was anticipated from the experience of one of us with the partial esterification of *r*-mandelic acid by *l*-borneol (*loc. cit.*). It had been found that when *r*-mandelic acid was heated with *l*-borneol, the unesterified acid was lævorotatory, or, in other words, that *l*-bornyl *d*-mandelate was more quickly formed than *l*-bornyl *l*-mandelate. Now Victor Meyer, Wegscheider, and others who have studied the saponification of isomeric aromatic esters, show clearly that, of two isomeric esters, the one which is the more quickly formed is also the more readily saponifiable. It was accordingly at first expected that, since *l*-bornyl *d*-mandelate is more quickly formed than *l*-bornyl *l*-mandelate, it would be saponified more quickly and that a dextrorotatory potassium salt would result from the saponification of *l*-bornyl *dl*-mandelate by an insufficiency of alkali. But it has just been pointed out that a lævorotatory potassium salt was actually obtained.

From subsequent experiments, however, on the racemisation phenomena during the saponification of optically active menthyl and bornyl esters by alkali (Trans., 1905, **87**, 1004), the deduction may be drawn that the formation of a lævorotatory potassium salt, to which reference has just been made, does not necessarily imply that the bornyl *l*-mandelate is saponified more quickly than the isomeric *d*-mandelate. During the progress of the saponification of *l*-bornyl *dl*-mandelate by an insufficiency of alkali, the optically active potassium mandelate formed is racemised to an extent which becomes less and less as the concentration of the hydroxyl ions diminishes and which is also, of course, dependent on the temperature conditions.

In order to prove that the interpretations previously advanced by the authors (*loc. cit.*) are correct, it was considered advisable to measure the velocities of saponification of each of the diastereoisomeric *l*-bornyl mandelates. Those compounds were accordingly prepared from *d*- and *l*-mandelic acids respectively, and had the following rotations in ethyl-alcoholic solutions:

l-Bornyl *d*-mandelate, $[\alpha]_D^{19}$ $+23{\cdot}2°$ ($c=4{\cdot}4425$).
l-Bornyl *l*-mandelate, $[\alpha]_D^{20{\cdot}5}$ $-84{\cdot}2°$ ($c=4{\cdot}6375$).

By taking the mean, the value $-30{\cdot}5°$ is obtained, a figure practically identical with that experimentally found for the specific rotation of *l*-bornyl *dl*-mandelate, namely, $-30{\cdot}4°$ ($t=20°$, $c=6{\cdot}6876$) (Trans., 1905, **87**, 1004). It is true that the rotations of the three isomerides were determined under slightly different conditions of concentration and temperature, but the influence of those factors on the values for specific rotation within the ranges examined appears to be very slight.

The results of the measurements quoted in the sequel show that *l*-bornyl *d*-mandelate is saponified more quickly than *l*-bornyl *l*-mandelate.

The opportunity was also taken of investigating the corresponding *l*-menthyl esters from the same standpoint. Here again it is shown by direct measurements with the respective esters that *l*-menthyl *d*-mandelate is saponified more quickly than *l*-menthyl *l*-mandelate.

The saponification constant was calculated by the formula for a reaction of the second order, namely,

$$k = \frac{2{\cdot}302 \times 1000}{T_\infty N_t} \log \frac{T_t(T_o - T_\infty)}{T_o(T_t - T_\infty)}.$$

Comparison of the saponification constants shows how much more quickly the bornyl esters are saponified than the menthyl esters. This difference in velocity of saponification is distinctly seen by comparison of the results of experiments II and XI, III and XII, V and XIII. Thus, to take one example from the results of experiments II and XI, where the temperature was 27° and the concentrations of the various solutions were practically identical, it will be seen that, after fifty-nine minutes, 67 per cent. of the bornyl *l*-mandelate was saponified, whilst, after sixty-eight minutes, only 37 per cent. of the menthyl ester was saponified. Again, contrasting experiments III and XII, where the saponification was conducted in each case more quickly at 27°, it will be seen, for example, that, after thirty-four minutes, 86 per cent. of the bornyl *l*-mandelate was saponified, whilst, in the same time, only 36 per cent. of the corresponding menthyl ester was saponified. In experiments V and XIII, where the temperature was 40°, 91 per cent. of the bornyl *l*-ester was saponified after 21·5 minutes, whereas only 55 per cent. of the menthyl *l*-ester was saponified after 22·5 minutes.

EXPERIMENTAL.

The *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate used were prepared as already described (Trans., 1904, **85**, 1249). Determina- of the melting points and specific rotations of these esters were in agreement with the values previously quoted.

l-Bornyl *d*-mandelate was prepared as follows. *d*-Mandelic acid, obtained by resolving the *r*-acid with morphine, was esterified by *l*-borneol according to the Fischer-Speier hydrogen chloride method. After the heating on a boiling-water bath had been continued for fourteen hours, the product was washed first with dilute sodium carbonate and finally with water, and then submitted to prolonged distillation in a current of steam until the excess of borneol had nearly all been removed. The residual viscous oil did not crystallise when exposed over sulphuric acid in a partial vacuum for three weeks; at the ordinary temperature it was very readily soluble in the commoner organic solvents. Its solution in ethyl alcohol crystallised when surrounded by a freezing mixture of solid carbon dioxide and alcohol and the crop, which separated, was drained off through a funnel surrounded by solid carbon dioxide. The crystals obtained in this manner became liquid at the ordinary temperature, and were freed from alcohol by heating; when nucleated by a crystal obtained by evaporating a small portion of the ethyl-alcoholic solution at the temperature of a mixture of solid carbon dioxide and ethyl alcohol, the oil solidified to a mass of minute, colourless, feathery needles.

l-*Bornyl* d-*mandelate*, $C_6H_5{\cdot}CH(OH){\cdot}CO_2{\cdot}C_{10}H_{17}$ (m. p. 50—51°), is practically insoluble in water and readily soluble in the commoner organic solvents at the ordinary temperature:

0·1820 gave 0·5021 CO_2 and 0·1390 H_2O. C = 75·2; H = 8·5.

$C_{18}H_{24}O_3$ requires C = 75·0; H = 8·4 per cent.

A determination of its specific rotation in ethyl alcohol gave the following result:

$$l = 2,\ c = 4{\cdot}4425,\ \alpha_D^{19}\ +2{\cdot}06°,\ [\alpha]_D^{19}\ +23{\cdot}2°.$$

In order to prepare the isomeric *l*-mandelate, the esterification of *l*-mandelic acid, obtained from amygdalin, was conducted as in the former case. After removal of free acid and borneol, the residual oil quickly solidified to a solid cake, which was crystallised by surrounding its ethyl-alcoholic solution with a freezing mixture of ice and salt.

l-*Bornyl* l-*mandelate*, $C_6H_5{\cdot}CH(OH){\cdot}CO_2{\cdot}C_{10}H_{17}$ (m. p. 78°), forms colourless glassy prisms, the behaviour of which towards solvents is similar to that of the ester already described:

0·2012 gave 0·5512 CO_2 and 0·1503 H_2O. C = 74·7; H = 8·4.

$C_{18}H_{24}O_3$ requires C = 75·0; H = 8·4 per cent.

A determination of its specific rotation in ethyl alcohol gave the result:

$$l = 2,\ c = 4{\cdot}6375,\ \alpha_D^{20{\cdot}5}\ -7{\cdot}81°,\ [\alpha]_D^{20{\cdot}5}\ -84{\cdot}2°.$$

Since the esters in question are saponified exceedingly slowly by aqueous alkalis, the measurements described were conducted with ethyl-alcoholic solutions. The ester was dissolved in a definite volume of ethyl alcohol, a definite volume of standard ethyl-alcoholic potassium hydroxide was then added, and 10 c.c. of the reaction mixture withdrawn at intervals. This amount was run into an excess of standard aqueous hydrochloric acid (25 c.c.) and the amount of free acid then estimated by titration against standard barium hydroxide with phenolphthalein as indicator.

The usual precautions as to constancy of temperature were maintained throughout. Before mixing the ester solution and the alkali, both were adjusted to the desired temperature in a thermostat; after mixing, 10 c.c. of the solution were immediately withdrawn and run into an excess of standard acid. In this manner the initial concentration of the ester in the solution undergoing saponification was determined. The final concentration of the ester was determined by heating 10 c.c. of the solution under a reflux condenser for one hour, adding standard acid and estimating the amount of free acid as usual.

EXPERIMENT I.

In this and in subsequent experiments:

Column a = time in minutes.
,, b = c.c. baryta required to neutralise excess of mineral acid.
,, c = c.c. acid used from 25 c.c.
,, d = percentage of ester saponified.

$T = 27°$; HCl = 0·03095 N (10 c.c. = 16·38 c.c. baryta).

l-*Bornyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	6·30	21·15	—
34	9·85	18·99	37*
105	14·00	16·45	81*
151	14·75	16·00	89*
∞	15·76	15·38	100

$k = 26·1$.

l-*Bornyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	6·32	21·14	—
36	9·82	19·00	39*
106	13·85	16·54	83*
151	14·68	16·04	92*
∞	15·37	15·62	100

$k = 27·8$.

EXPERIMENT II.

$T = 27°$; HCl = 0·03374 N (10 c.c. = 17·85 c.c. baryta).

l-*Bornyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	5·80	21·75	—
18	7·02	21·07	22
38	8·42	20·28	47*
59	9·55	19·65	67*
80	10·00	19·40	75*
109	10·50	19·12	84*
146	10·90	18·89	91*
208	11·00	18·84	93
∞	11·40	18·61	100

$k = 25·1$.

l-*Bornyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	5·73	21·79	—
19	7·06	21·04	24
38	8·50	20·24	50*
60	9·50	19·68	68*
81	10·07	19·36	79*
109	10·50	19·12	86*
146	10·85	18·92	93*
211	10·90	18·89	94
∞	11·25	18·70	100

$k = 27·2$.

EXPERIMENT III.

$T = 27°$; HCl = 0·149 N (10 c.c. = 38·45 c.c. baryta).

l-*Bornyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	16·23	20·78	—
11	17·65	20·41	40*
23	18·85	20·10	73*
34	19·30	19·98	86*
∞	19·80	19·85	100

l-*Bornyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	16·77	20·64	—
11	18·40	20·21	45*
23	19·60	19·90	77*
34	20·15	19·76	92*
∞	20·45	19·68	100

* The value for k is obtained by taking the mean of the values deduced from the experiments denoted by an asterisk.

Experiment IV.

$T = 27^\circ$; HCl = 0·149 N (10 c.c. = 38·45 c.c. baryta).

l-*Bornyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	18·83	20·10	—
9·5	20·07	19·78	33*
18	20·90	19·56	55*
36	21·95	19·29	84*
∞	22·57	19·13	100

General mean: $k = 16·6$.
(Calculated from III and IV).

l-*Bornyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	18·60	20·16	—
10	20·05	19·79	36*
18	21·07	19·52	62*
35·5	22·03	19·27	86*
∞	22·60	19·12	100

General mean: $k = 19·2$.
(Calculated from III and IV).

Experiment V.

$T = 40^\circ$; HCl = 0·07725 N (10 c.c. = 19·93 c.c. baryta).

l-*Bornyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	15·67	17·14	—
4	16·90	16·52	27*
8	18·20	15·87	56*
12·5	19·00	15·47	74*
21·5	19·77	15·08	91*
31·5	19·97	14·98	96
∞	20·17	14·88	100

$k = 81·2$.

l-*Bornyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	15·65	17·15	—
4	16·87	16·54	28*
8·5	18·20	15·87	58*
12·5	19·00	15·47	77*
21	19·65	15·14	92*
29·5	19·87	15·03	97
∞	20·00	14·96	100

$k = 84·9$.

Experiment VI.

$T = 27^\circ$; HCl = 0·03576 N (10 c.c. = 7·60 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	9·02	13·13	—
61	9·40	12·63	19*
143	9·95	11·91	46*
209	10·33	11·41	64*
∞	11·05	10·46	100

$k = 9·5$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	9·05	13·09	—
58	9·52	12·47	23*
141	10·20	11·58	55*
205	11·53	11·14	71*
∞	11·13	10·36	100

$k = 12·3$.

Experiment VII.

$T = 27^\circ$; HCl = 0·05411 N (10 c.c. = 11·50 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a	*b.*	*c.*	*d.*
0	13·78	13·02	—
71	14·43	12·45	35*
119	14·85	12·09	56*
182	15·23	11·76	75*
∞	15·70	11·35	100

$k = 10·1$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	13·73	13·06	—
71	14·63	12·28	42*
116	15·05	11·91	62*
180	15·40	11·61	78*
∞	15·87	11·20	100

$k = 12·1$.

* The value for k is obtained by taking the mean of the values deduced from the experiments denoted by an asterisk.

EXPERIMENT VIII.

$T = 27°$; HCl = 0·05411 N (10 c.c. = 11·50 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	11·15	15·31	—
104	12·22	14·38	52*
156	12·58	14·06	70*
220	12·80	13·87	80*
∞	13·20	13·52	100

$k = 9·4$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	11·18	15·28	—
102	12·45	14·18	59*
155	12·85	13·83	78*
218	13·05	13·65	88*
∞	13·32	13·42	100

$k = 12·1$.

EXPERIMENT IX.

$T = 27°$; HCl = 0·05411 N (10 c.c. = 11·45 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	9·12	17·03	—
41	9·68	16·55	25*
87	10·15	16·14	47*
145	10·63	15·72	70*
207	10·93	15·45	83*
324	11·13	15·28	92*
∞	11·30	15·13	100

$k = 8·9$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	9·20	16·97	—
40	10·00	16·27	37*
86	10·50	15·83	61*
145	10·83	15·54	76*
206	11·06	15·34	87*
324	11·26	15·17	96*
∞	11·35	15·09	100

$k = 12·0$.

EXPERIMENT X.

$T = 27°$; HCl = 0·05411 N (10 c.c. = 11·45 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	11·20	15·22	—
30	11·75	14·74	14*
62	12·43	14·14	32*
118	13·45	13·25	59*
160	13·95	12·82	72*
∞	15·02	11·88	100

$k = 8·8$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	11·35	15·09	—
30	12·07	14·46	18*
62	12·86	13·77	39*
118	13·90	12·86	65*
166	14·38	12·44	78*
∞	15·25	11·68	100

$k = 11·1$.

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* The value for k is obtained by taking the mean of the values deduced from the experiments denoted by an asterisk.

Experiment XI.

$T=27°$; HCl = 0·03384 N (10 c.c. = 17·9 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	4·80	22·32	—
47	6·10	21·59	25*
68	6·75	21·23	37*
97	7·60	20·75	53*
125	8·15	20·45	63*
154	8·65	20·17	73*
201	9·13	19·90	82*
314	9·60	19·64	91*
∞	10·07	19·37	100

$k=10·6$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	4·82	22·31	—
45·5	6·45	21·40	30*
66	7·10	21·03	43*
95	8·00	20·53	59*
124	8·67	20·16	72*
152	8·97	19·99	77*
199	9·27	19·82	83*
313	9·77	19·54	92*
∞	10·18	19·31	100

$k=12·6$.

Experiment XII.

$T=27°$; HCl = 0·149 N (10 c.c. = 38·45 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	16·50	20·71	—
12	16·95	20·59	13
22	17·27	20·51	22*
34	17·73	20·39	36*
46	18·27	20·25	52*
58	18·57	20·17	61*
71	18·90	20·08	71*
96	19·17	20·01	79*
∞	19·90	19·82	100

$k=5·0$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	16·45	20·72	—
12	17·07	20·56	17
22·5	17·90	20·34	40*
34	18·30	20·24	50*
46	18·80	20·11	64*
58·5	19·07	20·04	71*
71	19·30	19·98	77*
94	19·50	19·93	82*
∞	20·13	19·76	100

$k=6·9$.

Experiment XIII.

$T=40°$; HCl = 0·07725 N (10 c.c. = 19·93 c.c. baryta).

l-*Menthyl* l-*mandelate.*

a.	*b.*	*c.*	*d.*
0	15·83	17·06	—
7·5	16·60	16·67	17
15	17·60	16·17	40*
22·5	18·27	15·83	55*
30·5	18·87	15·53	68*
42·5	19·30	15·32	78*
65	19·87	15·03	91*
87	20·10	14·91	96
∞	20·30	14·82	100

$k=28·5$.

l-*Menthyl* d-*mandelate.*

a.	*b.*	*c.*	*d.*
0	15·90	17·02	—
8·5	17·20	16·37	29
15·5	18·17	15·88	50*
23·5	18·90	15·52	66*
31	19·30	15·32	75*
42·5	19·73	15·10	84*
65·5	20·15	14·89	93*
87·5	20·35	14·79	98
100	20·45	14·74	100

$k=35·6$.

---

* The value for k is obtained by taking the mean of the values deduced from the experiments denoted by an asterisk.

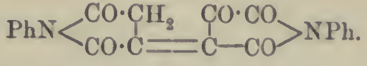
One of us (A. McK.) owes much to Prof. P. F. Frankland for helpful criticism and kindly encouragement in research during three years in the University of Birmingham, and desires to take this opportunity of expressing his gratitude.

THE UNIVERSITY,
BIRMINGHAM.

LXXIV.—*The Action of Ethyl Oxalate on Thioacetanilide and its Homologues.*

By SIEGFRIED RUHEMANN.

THE study of the behaviour of ethyl oxalate towards acetanilide and its analogues (see Ruhemann, Trans., 1906, **89**, 1236, 1847) led to the knowledge of compounds the representative of which, xanthoxalanil, has the formula



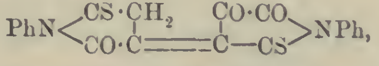
$$\mathrm{PhN}<\begin{array}{l}\mathrm{CO\cdot CH_2 \quad CO\cdot CO}\\ \mathrm{CO\cdot C{=\!=}C{-}CO}\end{array}>\mathrm{NPh}.$$

This constitution has been derived not only from the mode of formation of the substance, but also from the fact that, on hydrolysis with caustic potash, it yields dianilaconitic acid * which in turn furnishes aconitic acid on treatment with hydrochloric acid.

The results of this investigation have induced me to examine the reaction of thioacetanilide and its homologues with ethyl oxalate, and I have found that coloured compounds are formed which in composition differ from xanthoxalanil and its analogues only inasmuch as two of their oxygen atoms are replaced by sulphur. The substance which is produced from thioacetanilide, therefore, has the formula

$$C_{20}H_{12}O_3N_2S_2.$$

This fact leads to the conclusion that the constitution of the compound is analogous to that of xanthoxalanil, namely:

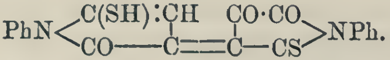


$$\mathrm{PhN}<\begin{array}{l}\mathrm{CS\cdot CH_2 \quad CO\cdot CO}\\ \mathrm{CO\cdot C{=\!=}C{-}CS}\end{array}>\mathrm{NPh},$$

---

* I had pointed out before (Trans., 1906, **89**, 1850) that a compound with this formula had been prepared by Michael (*Amer. Chem. J.*, 1887, **9**, 192) which, in melting point, differed by about 10° from the dianilaconitic acid obtained by me from xanthoxalanil. I have since prepared Michael's substance and find that the yield is very small, although the aqueous solution of the dianiline salt of aconitic acid had been kept for more than four weeks. A comparison of the two dianilaconitic acids has established the fact that they differ not only in their melting points, but also in their behaviour towards concentrated hydrochloric acid; this readily dissolves Michael's compound, as stated already by this chemist, whereas the other is insoluble.

and accordingly is to be called *dithioxanthoxalanil.* Similar formulæ must be assigned to the substances which are formed from the homologues of thioacetanilide. These compounds are highly coloured and sparingly soluble in most solvents. With regard to their colour I have noticed that they show similar differences from the corresponding compounds derived from acetanilide and its analogues, dithioxanthoxalanil being dark brown, whereas its homologues have a lighter shade. These thio-derivatives have no acidic properties, and in this respect resemble the other class of compounds; they differ, however, from the latter in their great stability towards alkalis. Whilst xanthoxalanil, on digestion with dilute caustic potash, is readily decomposed and yields dianilaconitic acid, dithioxanthoxalanil does not suffer a similar change under these conditions, but is transformed into its tautomeride. The fact that this substance is very soluble in dilute alkalis as well as alkali carbonates points to the formula:



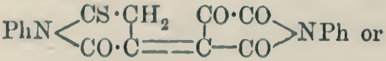
$$\mathrm{PhN}\left\langle\begin{array}{l}\mathrm{C(SH){:}CH}\quad\mathrm{CO{\cdot}CO}\\ \mathrm{CO{-\!-\!-}C{=\!=\!=}C{-}CS}\end{array}\right\rangle\mathrm{NPh.}$$

The formation of this compound is of some interest, because tautomeric forms of thioacetanilide and its homologues have not been obtained; P. Jacobson (*Ber.*, 1888, 21, 2627), indeed, stated that thioaceto-β-naphthalide, on rapidly cooling its alcoholic solution, crystallised in needles which changed into plates when left in the mother liquor for some time, but both kinds of crystals melted at the same temperature. This phenomenon was explained by the assumption that the different crystallographic forms corresponded to the tautomerides,

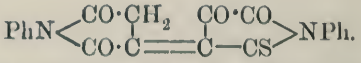
$$C_{10}H_7{\cdot}NH{\cdot}CS{\cdot}CH_3 \text{ and } C_{10}H_7N{:}C(SH){\cdot}CH_3,$$

but experimental proofs in support of this view have not been brought forward.

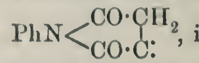
A more profound change in dithioxanthoxalanil takes place if this compound is boiled with dilute caustic potash for several hours, when one atom of sulphur is substituted by oxygen, and a substance, *thioxanthoxalanil,* is formed which, *a priori*, may be represented either by the formula

(1) 

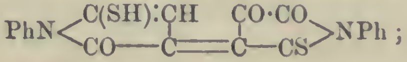
$$\mathrm{PhN}\left\langle\begin{array}{l}\mathrm{CS{\cdot}CH_2}\quad\mathrm{CO{\cdot}CO}\\ \mathrm{CO{\cdot}C{=\!=\!=}C{-}CO}\end{array}\right\rangle\mathrm{NPh}\text{ or}$$

(2) 

$$\mathrm{PhN}\left\langle\begin{array}{l}\mathrm{CO{\cdot}CH_2}\quad\mathrm{CO{\cdot}CO}\\ \mathrm{CO{\cdot}C{=\!=\!=}C{-}CS}\end{array}\right\rangle\mathrm{NPh.}$$

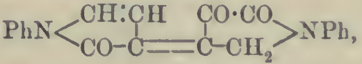
The fact, however, that this compound dissolves in sodium carbonate, whereas xanthoxalanil, which contains the group  $\mathrm{PhN}\left\langle\begin{array}{l}\mathrm{CO{\cdot}CH_2}\\ \mathrm{CO{\cdot}C{:}}\end{array}\right.$, is insoluble in this agent, points to the formula (1). Similar substances have been obtained from dithioxanthoxalo-p-toluidil and dithioxanthoxalo-β-naphthylamil. A complete decomposition of dithioxanthoxalanil is not effected until it is boiled with concentrated (60—70 per cent.) aqueous caustic potash, when aniline and oxalic acid are produced.

Of especial interest is the action of reducing agents on dithioxanthoxalanil; it has been shown previously (*loc. cit.*) that xanthoxaloxylidil, $C_{24}H_{20}O_5N_2$ (this compound had been chosen instead of xanthoxalanil on account of its solubility in glacial acetic acid), absorbs 6 atoms of hydrogen, and yields a colourless substance of the formula $C_{24}H_{26}O_5N_2$. Dithioxanthoxalanil, however, by the action of zinc dust and acetic acid, is transformed into a compound which has the composition $C_{20}H_{16}O_3N_2$, indicating that the sulphur is entirely replaced by hydrogen, and that no addition of hydrogen takes place. On the one hand, the fact that the substance is insoluble in cold alkalis or cold alkali carbonates, on the other that it is almost colourless, leads to the view that the substitution is accompanied by a change in the linking. Its formation is probably to be interpreted thus: dithioxanthoxalanil first changes into its tautomeride:



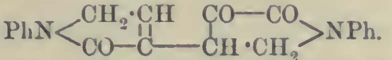
$$\mathrm{PhN}\Big<\begin{array}{l}\mathrm{C(SH){:}CH\quad CO{\cdot}CO}\\ \mathrm{CO{-}C{=}C{-}CS}\end{array}\Big>\mathrm{NPh};$$

this subsequently is transformed into:



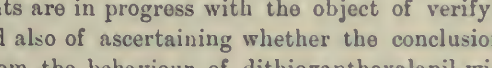
$$\mathrm{PhN}\Big<\begin{array}{l}\mathrm{CH{:}CH\quad CO{\cdot}CO}\\ \mathrm{CO{-}C{=}C{-}CH_2}\end{array}\Big>\mathrm{NPh},$$

which finally is reduced to



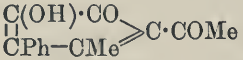
$$\mathrm{PhN}\Big<\begin{array}{l}\mathrm{CH_2{\cdot}CH\quad CO{-}CO}\\ \mathrm{CO{-}C{-}CH{\cdot}CH_2}\end{array}\Big>\mathrm{NPh}.$$

Experiments are in progress with the object of verifying this constitution, and also of ascertaining whether the conclusion which may be drawn from the behaviour of dithioxanthoxalanil with regard to the structure of the reduction product of xanthoxalanil is correct. The fact that the group ·CO·CO· is not altered in the course of the reduction of the thio-compound would suggest that it is not changed in the other case, and that the compound $C_{24}H_{26}O_5N_2$ is accordingly to be represented thus:



$$\mathrm{PhN}\Big<\begin{array}{l}\mathrm{CH(OH){\cdot}CH_2\quad CO{-}CO}\\ \mathrm{CO{-}CH{-}CH{\cdot}CH(OH)}\end{array}\Big>\mathrm{NPh}.$$

The reduction product, $C_{20}H_{16}O_3N_2$, of dithioxanthoxalanil is characterised by its behaviour towards alkalis or alkali carbonates. Although these reagents have no effect on the compound at the ordinary temperature, yet on boiling they transform it into a blue solid. This product is the alkali derivative of a cherry-red compound which is formed on adding dilute hydrochloric acid to the blue substance. I have not yet been able to complete the study of this red compound owing to the small yield of the reduction product $C_{20}H_{16}O_3N_2$, but there seems to be no doubt that it is isomeric with the latter substance. This reaction resembles the transformation which the yellow product of the reaction between acetylacetone and phenylpropiolyl chloride suffers under the influence of organic bases as well as sodium carbonate, and which yields the red substance



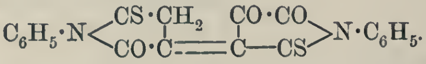
$$\begin{array}{l}\mathrm{C(OH)\cdot CO} \\ \| \\ \mathrm{CPh{-}CMe}\end{array}\!\!>\mathrm{C\cdot COMe}$$

(Ruhemann and Merriman, Trans., 1905, **87**, 1383). This also forms blue salts, as does Claisen and Ewan's oxalyldibenzyl ketone and triethyl anhydro-oxalaconitate (*loc. cit.*).

The analogy in the behaviour of these substances points to the view that the red compound which is formed from the reduction product of dithioxanthoxalanil under the influence of alkalis possesses a similar constitution. It differs from the other compounds of this type inasmuch as it is more stable both towards alkalis and alkali carbonates.

EXPERIMENTAL.

Dithioxanthoxalanil,



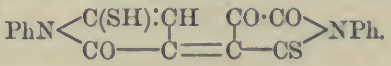
$$\mathrm{C_6H_5\cdot N}<\begin{array}{l}\mathrm{CS\cdot CH_2\quad CO\cdot CO} \\ \mathrm{CO\cdot C{=}{=}{=}C{-}CS}\end{array}>\mathrm{N\cdot C_6H_5}.$$

This substance is prepared by adding ethyl oxalate (20 grams) to sodium ethoxide (9 grams) suspended in dry benzene and mixing the solution with thioacetanilide (20 grams) dissolved in benzene. After a short time a yellow solid separates which undoubtedly is the sodium derivative of thioacetanilide. This disappears in the course of several hours, and a deep red solution is formed which, on standing overnight, sets to a semi-solid mass of red crystals. These have not been examined, because they are very hygroscopic, and on attempting to collect them are transformed into a gelatinous mass. On adding water to the product of the reaction, the solid readily dissolves, yielding a red solution which is separated from the benzene layer and treated with an excess of dilute hydrochloric acid; a cloudiness is produced which after a short time coalesces into a red solid. The precipitate is washed with water, then with alcohol, and dried in the steam-oven. The original aqueous filtrate and the dark alcoholic washings deposit a further amount of the substance in the course of a few days. The compound is insoluble in alcohol, fairly soluble in hot benzene, and very sparingly so in boiling glacial acetic acid; 5 grams require more than 1 litre of the solvent to yield a deep red solution, from which, on cooling, beautiful, brown prisms separate. The yield of the recrystallised substance amounts to about 50 per cent. of the weight of thioacetanilide. Dithioxanthoxalanil has no definite melting point; it darkens above 200° and decomposes at about 235° with evolution of gas:

0·1955 gave 0·4360 CO_2 and 0·0548 H_2O. C = 60·82 ; H = 3·11.
0·2396 ,, 14·8 c.c. moist nitrogen at 17° and 769 mm. N = 7·25.
0·2395 ,, 0·2843 $BaSO_4$. S = 16·30.
$C_{20}H_{12}O_3N_2S_2$ requires C = 61·22 ; H = 3·06 ; N = 7·14 ; S = 16·32 per cent.

Dithioxanthoxalanil is not attacked by hydrochloric acid even on boiling; it does not dissolve in either sodium carbonate or caustic potash at the ordinary temperature, but on digesting it with dilute alkalis (15 per cent.) it gradually dissolves and is transformed into

The Isomeride of Dithioxanthoxalanil,



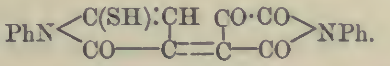
$$\mathrm{PhN}{<}\begin{array}{l}\mathrm{C(SH){:}CH\quad\;\; CO{\cdot}CO}\\ \mathrm{CO{-}{-}C{=}{=}C{-}CS}\end{array}{>}\mathrm{NPh.}$$

This is isolated by adding dilute hydrochloric acid to the yellow alkaline solution, when it is precipitated as a red solid. After being washed with water, it is dissolved in boiling alcohol; the solution, on cooling, deposits long, red needles which do not melt, but decompose at about 195° :

0·2012 gave 0·4495 CO_2 and 0·0569 H_2O. C = 60·93 ; H = 3·14.
0·1970 ,, 0·4420 ,, ,, 0·0545 ,, C = 61·19 ; H = 3·07.
0·2302 ,, 14·4 c.c. moist nitrogen at 18° and 758 mm. N = 7·20.
0·2105 ,, 0·2507 $BaSO_4$. S = 16·35.
$C_{20}H_{12}O_3N_2S_2$ requires C = 61·22 ; H = 3·06 ; N = 7·14 ; S = 16·32 per cent.

The isomeride of dithioxanthoxalanil is moderately soluble in boiling alcohol, more readily so in hot glacial acetic acid; it dissolves in caustic potash or in sodium carbonate, yielding yellowish-red solutions.

Thioxanthoxalanil,



$$\mathrm{PhN}{<}\begin{array}{l}\mathrm{C(SH){:}CH\quad\;\; CO{\cdot}CO}\\ \mathrm{CO{-}{-}C{=}{=}C{-}CO}\end{array}{>}\mathrm{NPh.}$$

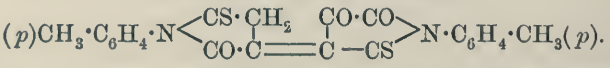
This compound is formed on boiling dithioxanthoxalanil with aqueous caustic potash (15—20 per cent.) in a flask with a reflux condenser. It is necessary to continue the heating for some time. The transformation is complete after six hours' boiling, otherwise a mixture of thioxanthoxalanil and the tautomeride of dithioxanthoxalanil is produced. Their separation may be effected by means of boiling alcohol, in which the latter substance is fairly soluble, whereas thioxanthoxalanil is almost insoluble. The yellowish-red solution, when treated with hydrochloric acid, evolves hydrogen sulphide and yields a gelatinous precipitate which, after being washed with water, is dried on porous porcelain. The substance dissolves in a large quantity of boiling glacial acetic acid, and, on cooling, crystallises in shiny, orange plates which melt and decompose at 216—218° :

0·2053 gave 0·4797 CO_2 and 0·0603 H_2O. C = 63·72; H = 3·26.
0·2062 ,, 13·6 c.c. moist nitrogen at 18° and 746·5 mm. N = 7·48.
0·2460 ,, 0·1510 $BaSO_4$. S = 8·43.
$C_{20}H_{12}O_4N_2S$ requires C = 63·83; H = 3·19; N = 7·44; S = 8·51 per cent.

Thioxanthoxalanil dissolves in aqueous sodium carbonate on warming to yield a pale yellow solution, but it is insoluble in concentrated hydrochloric acid even on boiling.

The formation of this substance is not accompanied by the production of aniline and oxalic acid, and this fact indicates that a complete decomposition is not effected by the dilute alkali; this does not take place until dithioxanthoxalanil is boiled with concentrated (about 75 per cent.) aqueous caustic potash. The brown crystals first dissolve, yielding a red solution which shortly deposits a yellow solid; this afterwards disappears, and a green liquid is produced which retains an oil in suspension. After one hour's heating, the product of the reaction is agitated with ether; this extracts an oil which has been recognised as aniline. The alkaline layer gives with dilute hydrochloric acid a gelatinous precipitate which dissolves in ether and, on removal of the solvent, is left behind as a green resin. The remaining acid solution contains oxalic acid.

Dithioxanthoxalo-p-*toluidil*,

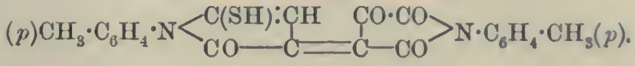


$$(p)CH_3\cdot C_6H_4\cdot N\!<\!\begin{array}{llll} CS\cdot & CH_2 & CO\cdot CO & \\ & | & | & \\ CO\cdot & C = & C - CS & \end{array}\!>\!N\cdot C_6H_4\cdot CH_3(p).$$

Thioaceto-*p*-toluidide, which had been prepared according to Jacobson and Ney's directions (*Ber.*, 1889, **22**, 906), is not so readily soluble in benzene as thioacetanilide. On adding this substance (33 grams), dissolved in hot benzene, to the solution which is formed by mixing dry sodium ethoxide (13·6 grams) suspended in benzene, and ethyl oxalate (29·5 grams), a precipitate is formed in this case also; this dissolves after several hours, yielding a deep red solution which, however, on standing overnight, does not deposit a solid. It is agitated with water, and the aqueous layer is treated with an excess of hydrochloric acid, when a cloudiness is produced which, after a short time, coalesces into a red solid; this dissolves in much boiling glacial acetic acid, and, on cooling, crystallises in bunches of dark red needles which are paler in colour than dithioxanthoxalanil. The substance melts and decomposes at about 248°:

0·2020 gave 0·4645 CO_2 and 0·0708 H_2O. C = 62·71; H = 3·89.
0·2080 ,, 11·6 c.c. moist nitrogen at 16° and 775 mm. N = 6·63.
$C_{22}H_{16}O_8N_2S_2$ requires C = 62·85; H = 3·81; N = 6·67 per cent.

Thioxanthoxalo-p-*toluidil*,



$$(p)CH_3\cdot C_6H_4\cdot N<\begin{array}{l}C(SH)\colon CH \qquad CO\cdot CO\\ CO\text{—}C\text{==}C\text{—}CO\end{array}>N\cdot C_6H_4\cdot CH_3(p).$$

Dithioxanthoxalo-*p*-toluidil dissolves in dilute aqueous caustic potash, but not so readily as dithioxanthoxalanil; it yields a dark red solution which, on treatment with hydrochloric acid, forms a red precipitate, and at the same time hydrogen sulphide is evolved. This indicates that the formation of the isomeride of the dithio-derivative is accompanied by the production of thioxanthoxalo-*p*-toluidil. This conclusion is corroborated by the fact that the red precipitate is a mixture. I have not been able to separate it, and on analysis of the product, which had been recrystallised from alcohol, the following results were obtained:

0·2004 gave 0·4683 CO_2 and 0·0725 H_2O. C = 63·73; H = 4·01; which lie between the numbers required for the two substances:

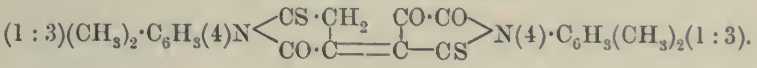
$C_{22}H_{16}O_3N_2S_2$ requires C = 62·85; H = 3·81,
$C_{22}H_{16}O_4N_2S$ „ C = 65·34; H = 3·96 per cent.

In order to prepare thioxanthoxalo-*p*-toluidil in a pure state, the dithio-compound is boiled with an excess of caustic potash (15—20 per cent.) for five to six hours; the alkaline solution, when cold, is mixed with dilute hydrochloric acid, when hydrogen sulphide is evolved and a yellow solid is precipitated. This, after being washed with water, is dried on a porous plate and then dissolved in boiling alcohol, in which it is only sparingly soluble; on cooling, shiny, orange plates separate which are paler in colour than the corresponding thioxanthoxalanil, and melt at 226—228° with decomposition:

0·2018 gave 0·4815 CO_2 and 0·0722 H_2O. C = 65·07; H = 3·97.
$C_{22}H_{16}O_4N_2S$ requires C = 65·34; H = 3·96 per cent.

This substance, like thioxanthoxalanil, readily dissolves in alkalis as well as alkali carbonates.

Dithioxanthoxalo-m-*xylidil*.

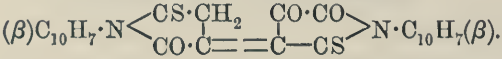


$$(1:3)(CH_3)_2\cdot C_6H_3(4)N<\begin{array}{l}CS\cdot CH_2 \qquad CO\cdot CO\\ CO\cdot C\text{==}C\text{—}CS\end{array}>N(4)\cdot C_6H_3(CH_3)_2(1:3).$$

The solution which is formed on adding ethyl oxalate (11 grams) to sodium ethoxide (5 grams), suspended in benzene, when mixed with thioaceto-*m*-xylidide (13 grams) dissolved in benzene (it is readily soluble in this solvent), yields a precipitate which disappears in the course of a day, forming a dark red solution. This does not deposit a solid, but on treating the aqueous extract with hydrochloric acid an oily product is precipitated which, on standing, sets to a dark brown solid. This is more soluble in boiling glacial acetic acid than the former dithio-derivative, and, on cooling, crystallises in brick-red, prismatic plates which soften at 225° and melt at about 235° with decomposition :

0·2002 gave 0·4710 CO_2 and 0·0820 H_2O. $C=64·16$; $H=4·55$.
0·2270 „ 12·2 c.c. moist nitrogen at 15° and 773 mm. $N=6·40$.
0·2587 „ 0·2722 $BaSO_4$. $S=14·45$.
$C_{24}H_{20}O_3N_2S_2$ requires $C=64·28$; $H=4·46$; $N=6·25$; $S=14·29$ per cent.

Dithioxanthoxalo-β-naphthylamil,



$$(\beta)C_{10}H_7\cdot N\Big<\begin{matrix}CS\cdot CH_2 & CO\cdot CO\\ CO\cdot C= & =C-CS\end{matrix}\Big>N\cdot C_{10}H_7(\beta).$$

This substance is formed in the same way as the former dithio-compound, using β-naphthylthioacetamide. In order to dissolve the amide, a large quantity of hot benzene is required; the precipitate obtained on adding this solution to the mixture of sodium ethoxide and ethyl oxalate gradually dissolves, and the solution, in the course of a day, deposits a red solid which is soluble in water. On adding hydrochloric acid to the aqueous layer, a red precipitate is formed which is insoluble in alcohol or glacial acetic acid, but dissolves in boiling nitrobenzene and, on cooling, crystallises in small red needles. These are separated from the dark coloured mother liquor by filtration and frequently washed with boiling alcohol. The substance does not melt, but begins to darken at about 250° and finally turns black :

0·2020 gave 0·5065 CO_2 and 0·0625 H_2O. $C=68·38$; $H=3·43$.
0·2123 „ 10·4 c.c. moist nitrogen at 19° and 770 mm. $N=5·70$
$C_{28}H_{16}O_3N_2S_2$ requires $C=68·29$; $H=3·25$; $N=5·69$ per cent.

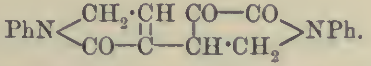
This compound reacts with caustic potash in the same way as the dithio-derivatives. On boiling with the alkali (15 per cent.), it dissolves with the exception of a small quantity of a black solid; the dark colour of the solution then changes to yellowish-red. After four hours' heating, the solution is poured off from the solid which adheres to the sides of the flask and treated with dilute hydrochloric acid, when hydrogen sulphide is evolved and a red precipitate is formed. This is insoluble in alcohol or glacial acetic acid; it dissolves in boiling nitrobenzene, but is decomposed at the same time, and the solution, on cooling, does not deposit any solid. I have not analysed this substance, but there cannot be any doubt that it is thioxanthoxalo-β-naphthylamil.

Reduction of Dithioxanthoxalanil.

The dark red solution of dithioxanthoxalanil in glacial acetic acid is rapidly decolorised by zinc dust. Instead of bringing the dithio-compound into solution, which requires a considerable volume of the solvent, it is more convenient to boil the substance (8 grams) with a smaller quantity of glacial acetic acid (about 500 c.c.), and to add gradually an excess of zinc dust to the suspension, when in a few minutes the action is complete. The product is filtered while hot through asbestos, and the residue again extracted with acetic acid. The filtrate, which has a pale yellow colour, cannot be concentrated by distillation of the acid, because it turns red; it is therefore mixed with water, when a gelatinous substance is precipitated. This is washed with water, dried on a porous plate, and dissolved in boiling glacial acetic acid; the solution, on cooling, deposits grey, shiny plates which do not melt, but begin to darken at about 240° and finally turn black:

0·2015 gave 0·5330 CO_2 and 0·0885 H_2O. $C = 72·14$; $H = 4·88$.
0·2160 ,, 15·8 c.c. moist nitrogen at 18° and 768 mm. $N = 8·53$.
$C_{20}H_{16}O_3N_2$ requires $C = 72·30$; $H = 4·82$; $N = 8·43$ per cent.

The substance is insoluble in benzene, sparingly soluble in hot alcohol, more readily so, however, in boiling glacial acetic acid. Its constitution, as stated before (p. 799), is probably to be represented thus:



$$\mathrm{PhN}<\begin{array}{ccccc}\mathrm{CH_2{\cdot}CH} & & \mathrm{CO} & \text{—} & \mathrm{CO}\\ \quad\| & & | & & \\ \mathrm{CO{-}C} & \text{—} & \mathrm{CH{\cdot}CH_2} & & \end{array}>\mathrm{NPh}.$$

A similar compound is formed from dithioxanthoxalo-*p*-toluidil, which crystallises from glacial acetic acid in nearly colourless prisms, and on heating behaves like the former substance. The yield in both cases is very small.

The compound, $C_{20}H_{16}O_3N_2$, which is produced on reduction of dithioxanthoxalanil (and the corresponding substance obtained from the homologue of the dithio-derivative) is not soluble either in sodium carbonate or caustic soda at the ordinary temperature, but on boiling with these reagents yields a blue substance; this, in the presence of alkali, is sparingly soluble in water; it dissolves, however, fairly readily when the alkali has been washed away. The blue solid and its solution, on treatment with hydrochloric acid, turn red, and yield a compound which by alkalis is transformed back again into its blue salts. The red substance is insoluble in alcohol or glacial acetic acid, but dissolves in hot nitrobenzene, and on cooling separates in reddish-brown crystals. The small yield of the reduction product of dithioxanthoxalanil has prevented me from studying more closely the remarkable transformation it undergoes when treated with alkalis, but I am continuing this investigation in order to prove the relation of the substance which is thus formed to the compounds with similar properties.

GONVILLE AND CAIUS COLLEGE,
CAMBRIDGE.

LXXV.—*The Magnetic Rotation of Hexatriene,* $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, *and its Relationship to Benzene and other Aromatic Compounds: also its Refractive Power.*[*]

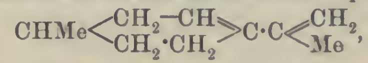
By SIR WILLIAM HENRY PERKIN.

IN a paper on magnetic rotatory power, especially of aromatic compounds (Trans., 1896, **69**, 1025), attention is repeatedly drawn to the very high rotations of aromatic compounds, and the difficulty of finding a satisfactory explanation of these abnormally high values is especially emphasised. That the values for aromatic compounds should be much higher than those of aliphatic saturated compounds was to be expected, because rotations increase for every unsaturated grouping which the substance contains, but that they should be so abnormally high as they have been found to be, admitted, at that time, of no satisfactory explanation. The examination of hexylene, diallyl, and dipropargyl showed that their magnetic rotations appeared to be about normal, and the value for each unsaturated grouping rose only slightly as the number of these groupings increased (Trans., 1895, **67**, 255[†]). The two acetylene groupings in dipropargyl, $CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}CH$, also seemed to act like four ordinary unsaturated groups, but when dipropargyl was compared with its isomeride benzene, a very striking difference in rotation was observed, the value for dipropargyl (10·435) being much lower than that of benzene (11·284). It was supposed at the time that this difference was due, in some way, to the ring formation of benzene.

[*] Compare J. W. Brühl (Trans., 1907, **91**, 115, and *Ber.* 1907, **40**, 878).

[†] Griner (*Ann. Chim. Phys.*, 1892, [vi], **26**, 323, 346) has shown that diallyl and dipropargyl as ordinarily prepared are not pure products, but contain small quantities of isomeric hydrocarbons, so that the true magnetic rotations of the pure substances may be found to differ to some slight extent from those given in this paper.

That this was the chief reason became, however, very doubtful when the remarkable observation was made that *d*-$\Delta^{3\cdot8(9)}$-*p*-menthadiene,



$$CHMe{<}\begin{matrix}CH_2{-}CH\\CH_2{\cdot}CH_2\end{matrix}{\gg}C{\cdot}C{\ll}\begin{matrix}CH_2\\Me\end{matrix},$$

which contains two unsaturated groupings in conjunction, yielded abnormally high numbers for the magnetic rotation (Trans., 1906, **89**, 854). This result seemed to point to the possibility that the high rotations of benzene derivatives and other substances containing unsaturated groups in conjunction was, in fact, chiefly due to the presence of these groups.

In order to test this supposition, it seemed very desirable, in the first place, to examine some open chain compounds in order that the effect of association might be determined without any disturbing influence due to ring formation. Fortunately this was rendered possible by the discovery of P. van Romburgh and W. van Dorssen (*Proc. K. Akad. Wetensch., Amsterdam*, 1905, **8**, 565) of *hexatriene*, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, which contains three contiguous unsaturated groups, and I have to thank these gentlemen for their kindness in placing about 25 c.c. of this rare substance at my disposal for the purpose of examination. Two separate determinations of the magnetic rotation of the freshly fractionated hydrocarbon were made and these gave concordant results, the average value being 12·196. This is a remarkably high number, higher indeed than that of benzene itself (11·284), from which hexatriene only differs in containing 2 atoms of hydrogen more.

The difference in the formulæ of hexatriene and benzene is simply the difference of ring formation due to the loss of two atoms of hydrogen, and is exactly the same as the difference between hexane and hexamethylene; the latter value has been determined experimentally and found to be 0·982 (Trans., 1902, **81**, 295).

If we subtract this difference from hexatriene, we obtain a value for the magnetic rotation of benzene based on the assumption that benzene contains three unsaturated groupings.

Magnetic rotation of hexatriene	12·196
Difference for ring formation	0·982
Calculated rotation of benzene...............	11·214

It is interesting to note that this number is practically identical with that actually found for the rotation of benzene (11·284), and this fact seems to point to two important conclusions, namely, that benzene contains three contiguous unsaturated groupings (Kekulé's formula), and secondly that these have substantially the same value as in the case of open chain compounds. Another set of comparisons which point in the same direction is the following:

Hexatriene	12·196	Benzene	11·284
Hexane	6·646	Hexamethylene	5·664
Difference	5·550	Difference	5·620

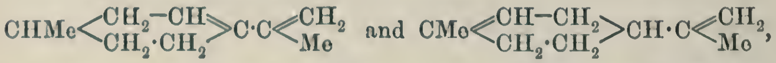
These comparisons of such widely differing substances are, moreover, interesting for another reason, namely, because the difference (5·6 approx.) gives us a reliable value for the association of three double linkings.* In this connexion, the following comparisons of hexatriene, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, and diallyl, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, serve to show the remarkable effect which is produced when two unsaturated groups become united by means of a third. In the formula for diallyl, there are two unsaturated groups separated by $\cdot CH_2{\cdot}CH_2\cdot$; in hexatriene this intermediate group is displaced by $\cdot CH{:}CH\cdot$, a displacement which, in ordinary circumstances, would cause a rise of rotation of about 0·730. The actual determinations gave, however, the following figures:

Hexatriene	12·196
Diallyl	8·420
Difference	3·776

and it is seen that the rise in rotation is about three whole numbers more than would have been the case had the unsaturated groupings not been associated.

In making some attempt to estimate approximately the effect of association in connexion with unsaturated groupings, the following points are worthy of consideration.

d-$\Delta^{3\cdot 8(9)}$-*p*-Menthadiene and *d*-limonene,



$$\mathrm{CHMe}<\substack{\mathrm{CH_2{-}CH}\\ \mathrm{CH_2{\cdot}CH_2}}\geqslant\mathrm{C{\cdot}C}\leqslant\substack{\mathrm{CH_2}\\ \mathrm{Me}}\quad\text{and}\quad\mathrm{CMe}\leqslant\substack{\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}}>\mathrm{CH{\cdot}C}\leqslant\substack{\mathrm{CH_2}\\ \mathrm{Me}},$$

both contain two unsaturated groupings, and are exactly similarly constituted, with the exception that in *d*-menthadiene the two unsaturated groupings are associated, whereas in *d*-limonene they are separated by the group $\cdot CH_2{\cdot}CH_2\cdot$. The difference in the observed rotations of these two terpenes is 1·815, or 0·907 for each associated unsaturated group, as seen from the following comparison of their respective rotations:

---

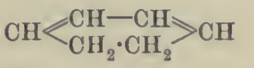
* By the value for an associated double linking is understood the number which represents the conversion of the group $\cdot CH_2{\cdot}CH_2\cdot$ into an *associated* double linking $\cdot CH{:}CH\cdot$. The actual effect due to association would be obtained by subtracting from this the value for unsaturation (that is, the value obtained when the group $\cdot CH_2{\cdot}CH_2\cdot$ is converted into an *ordinary* unsaturated group).

d-$\Delta^{3\cdot8(9)}$-p-Menthadiene	13·061
d-Limonene	11·246
	2)1·815
	0·907

If 0·730 (the ordinary value for unsaturation) is added to this, we obtain 1·637 as the rise in rotation due to the conversion of a group, $\cdot CH_2\cdot CH_2\cdot$, into an associated double linking, $\cdot CH\colon CH\cdot$. It is interesting to note that this value is considerably less than that observed in the case of *three* associated double linkings, because, if the difference between hexatriene and hexane (namely, 5·550, see above) is divided by three, we obtain 1·85 as the value for each of the three double linkings in hexatriene.

In the case of d-$\Delta^{3\cdot8(9)}$-p-menthadiene, we have the interesting condition that one of the associated double linkings is situated within whilst the other is outside the ring, and it is evident that in these circumstances there is a similar rise in value to that observed when both associated linkings are inside or outside a ring, although there may, of course, be some slight difference in the amount of the rise.

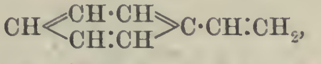
The only case of the association of two unsaturated groupings within the ring which has been directly measured is the case of $\Delta^{1:3}$-dihydrobenzene,



$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH{-}CH}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}\right\rangle\mathrm{CH}$$

(Crossley, Trans., 1904, 85, 1418), which was found to have a rotation of 8·093. If the value for hexamethylene (5·664) is deducted from this, we obtain 2·429 as the value of the two associated double linkings or 1·218 for each, and this is perhaps a rather smaller value than might have been expected. No open chain compound has, so far, been measured which contains two associated double linkings, but a substance of this type is in the course of preparation, and the determination of its magnetic rotation should yield very interesting results.

In comparing d-$\Delta^{3\cdot8(9)}$-p-menthadiene with hexatriene it was indicated that rotation rises in a remarkable manner as the number of associated double linkings in the molecule increases, and that this rise quickly becomes enormous may be shown from the following considerations. Styrene,

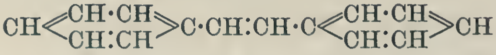


$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CH\cdot CH}\\ \mathrm{CH\colon CH}\end{matrix}\right\rangle\mathrm{C\cdot CH\colon CH_2},$$

is benzene to which an associated double linking has been added, and the effect of this addition may be estimated as follows.

When styrene is compared with ethylbenzene, it is clear that the former is derived from the latter by the conversion of the group $\cdot CH_2\cdot CH_2\cdot$ into the associated double linking $\cdot CH{:}CH_2$.

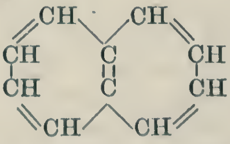
If, then, we deduct the rotation of ethylbenzene (13·382) from that of styrene (16·041) we obtain the high figure 2·659 as the result of this change. This number does not, of course, represent the value of the additional associated double linking; it is obviously the increase in value of the three double linkings contained in benzene by association with a fourth. It has already been pointed out that the three associated double linkings in benzene have a value of 5·620 or 1·87 for each, and therefore the value of the four associated double linkings in styrene may be calculated as 8·279 (5·620 + 2·659) or 2·07 for each. Clearly then there has been a considerable rise in the value for each associated linking in passing from a compound containing three to one containing four such linkings. If the molecule contains still more associated double linkings, the rise in rotation increases enormously with the number of such linkings and, in this connexion, the case of stilbene,



$$CH{<}\begin{matrix}CH\cdot CH\\CH{:}CH\end{matrix}{>}C\cdot CH{:}CH\cdot C{<}\begin{matrix}CH\cdot CH\\CH{:}CH\end{matrix}{>}CH$$

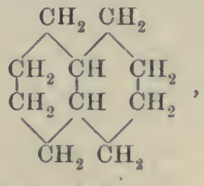
which contains seven associated double linkings, is worthy of special attention. The rotation of stilbene is 33·143, and if from this we deduct the rotation of dibenzyl, 24·997, we obtain 8·146 as the result of introducing the seventh associated double linking. The total rise in rotation due to the seven double linkings is therefore 19·386 (8·146 + 11·240 from two benzene rings) or about 2·77 for each.

Another interesting case is that of naphthalene, the enormous rotation of which is probably of a similar kind to that suggested in considering the other cases mentioned above. If naphthalene is represented by the formula



it contains five associated double linkings, and is derived from benzene by the addition of two such linkings. The rotation of naphthalene is 25·125, and if the value of benzene, −2H, 10·776, is deducted from this we obtain the enormous value 14·349 for the introduction of the grouping $\cdot CH{:}CH\cdot CH{:}CH\cdot$. The actual value of each of the five associated double linkings in naphthalene may be roughly calculated thus. The rotation of hexamethylene is 5·664 and two-thirds of this, or 3·776, represents the value of $\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot$ in the ring.

The value for decahydronaphthalene,



calculated on this basis is therefore

Hexamethylene −2H	5·156
$\cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2$	3·776
Decahydronaphthalene............	8·932

If this is deducted from the rotation of naphthalene (25·125) we obtain 16·193 as the value for five associated double linkings or 3·24 for each of these. One of the most interesting examples of the rise due to association is brought to light when a comparison is made between the rotations of benzene and diphenyl. Diphenyl is produced when 2 molecules of benzene unite with the loss of 2 atoms of hydrogen. The rotation of diphenyl is 25·304, and if from this we deduct the value of 2 molecules of benzene less 2 atoms of hydrogen, 22·060, we have a rise of rotation of 3·244, which can only be due to the association of the two sets of three double linkings which is brought about when the two phenyl groups combine.

In other words, the value of each of the three double linkings in benzene has risen from 1·87 to 2·41 in diphenyl simply as the result of causing the two sets of three to combine and become six.

Leaving out the case of naphthalene, which is not quite comparable, the above deductions may be conveniently summarised and we then obtain a clear representation of the remarkable fact that rise of rotation due to association increases more or less uniformly with the number of associated linkings contained in the molecule.

In dihydrobenzene, *two* associated double linkings have a value of 1·22 each; in benzene, *three* have the value of 1·87 each; in styrene, *four* have the value of 2·07 each; in diphenyl *six* have the value of 2·61 each, and in stilbene, *seven* have the value of 2·77 each.

In my paper on "The Magnetic Rotatory Power of Aromatic Compounds" (Trans., 1896, 69, 1161) attention was repeatedly called to the "screening" effect which is observed when a group enters the molecule in such a way as to prevent double linkings from becoming associated. The value of $C_6H_5\cdot$ in benzene is 11·03; when two of these groups are united, in diphenylmethane, by a $\cdot CH_2 \cdot$ group, the value of each, $C_6H_5\cdot$ rises to 11·411.

When, however, the intervening $\cdot CH_2 \cdot$ in diphenylmethane is removed, so that the two phenyl groups come into direct union, the influence of each $C_6H_5\cdot$ group rises to 12·657.

It seems therefore that when the associated double linkings are screened by $\cdot CH_2\cdot$, they still exert a certain although comparatively slight influence on the rotation of the molecule. When the screening group contains oxygen, the effect is still more marked, as is evident from the consideration of the two following cases. In allyl benzoate, $CH_2\colon CH\cdot CH_2\cdot CO_2\cdot C_6H_5$, the screening effect of the group $\cdot CH_2\cdot CO_2\cdot$ is so pronounced that the group $CH_2\colon CH\cdot$ is scarcely influenced by the presence of the phenyl group and has an almost normal value, and again in the case of phenyl allyl ether, $C_6H_5\cdot O\cdot CH_2\cdot CH\colon CH_2$, the group $\cdot O\cdot CH_2\cdot$ greatly minimises the effect of the phenyl group on the unsaturated grouping $\cdot CH\colon CH_2\cdot$ (Trans., 1896, **69**, 1141).

Attention had previously been called (Trans., 1896, **69**, 1095, 1098, 1162) to the very remarkable difference which had been observed in the influence of the $\cdot NO_2$, NH_2, and $\cdot NMe_2$ groups, when introduced into the benzene nucleus. The NO_2 group, in which nitrogen is quinquevalent, causes a diminution in the rotation of benzene, whereas the NH_2 and NMe_2 groups with tervalent nitrogen raise the rotation to an extraordinary extent, as the following comparisons show:

	Mag. rot.		Mag. rot.
Nitrobenzene	9·361	Aniline...... ..	16·076
Benzene	11·284	Benzene	11·284
Difference	−1·923	Difference......	+4·792

The cases of dimethylaniline (22·888) and dimethyl-β-naphthylamine (47·377) are even more remarkable, because in the first instance the introduction of the $\cdot NMe_2$ group into benzene raises the rotation by 11·604, and in the second that of naphthalene by 22·252, whereas this group, in the aliphatic series, has only a very small rotation, as is shown by the fact that the rotation of ethylamine (dimethylamine has not been measured) is only 3·609. It seems probable that the large effect produced by the introduction of the NH_2 and NMe_2 groups is due, as in the case of the introduction of the $\cdot CH\colon CH_2\cdot$ group (p. 810), in part at least, to the association of the unsaturated groups with the associated double linkings of the nucleus. This view is borne out by the observation that the hydrochlorides of aniline and dimethylaniline in which the nitrogen atoms have become saturated have in the case of aniline a rotation very little higher than that of this base, and in dimethylaniline a considerably lower rotation (aniline 16·076 aniline hydrochloride = 16·394; dimethylaniline 22·888, dimethylaniline hydrochloride = 18·326). When therefore the value of hydrogen chloride (2·245) is taken into account, it is seen that the addition with consequent saturation of the nitrogen atom has produced a remarkable lowering in the rotation. It is worth noting that the introduction of a second NO_2, NH_2, or NMe_2 group does not act like the first. In the case of the second NO_2 group there is no longer a reduction, but a slight rise in the rotation, and in the case of the second NH_2 and NMe_2 groups the rise is much smaller than in the case of the first introduction.

Comparison of the Refractive Power of Hexatriene with that of Benzene.

The careful examination of freshly distilled hexatriene, C_6H_8, has shown that the refraction, and especially the dispersion, of this substance are both considerably higher than the calculated.

Refraction $\frac{\mu_a - 1}{d}p$.	Dispersion $H_\gamma - H_a$.
51·650	4·472

The calculated refractive power of a substance, C_6H_8, containing three double linkings is 47·300, or 4·350 less than was actually found, and it is remarkable that the dispersion of benzene, containing 2 atoms of hydrogen less, is only 2·426, or not much more than half that of hexatriene.

The comparison of the above values for hexatriene with those of benzene show that the differences do not run parallel with the magnetic rotation results. As stated on p. 808, the differences in rotation between hexatriene and hexane (5·550) and between hexamethylene and benzene (5·620) are practically the same. But when a similar comparison of the refractive powers is made an entirely different result is obtained.

	H_a.		H_a.
Hexatriene......	51·650	Benzene	44·087
Hexane	48·630	Hexamethylene ...	45·824
Difference	+3·020		−1·737

It is very difficult to account for these striking differences, but it may be stated generally that, although there is often a similarity between refractive powers and magnetic rotations, many cases have been observed in which very little relationship seems to exist between the two sets of values. Thus, for example, the magnetic rotation of benzene is *much larger* than that calculated on the assumption that it is a compound, C_6H_6, containing three double linkings of the *ordinary value*, whereas the refractive power is *actually less* than that calculated on the same basis. Similar peculiarities have been observed in a number of other cases, and these tend to show that magnetic rotation not infrequently detects differences which the determination of the refractive power fails to reveal.

EXPERIMENTAL.

The specimen of hexatriene (about 25 c.c.) was received in a sealed glass flask. When opened, it was found that a few drops of the substance, when placed on bibulous paper, did not entirely evaporate, but left an oily stain; it had therefore apparently polymerised to some extent, as its original boiling point was 79·5—81°. On distillation, most of it passed over between 77° and 80°, chiefly 78—80°. The temperature was then allowed to rise to 95°, when the distillation almost ceased, about 3 c.c. of a viscid oily product being left behind. The fraction 77—80° was examined as to its density, magnetic rotation, and refractive power. Seventeen days later this product was re-fractionated; it then passed over mostly between 77·5° and 79°, only a small amount of polymerised product being left behind. This fraction was also examined, and was found to have practically the same density, magnetic rotation, and refractive power as the previous product. On keeping this for several weeks it underwent scarcely any change, only a minute quantity of polymerised product being formed. It almost appears as though the original product contained two isomeric hydrocarbons, one polymerising quickly and the other slowly, the specimen I examined consisting of the latter, but as very small changes of conditions often greatly influence the rate of polymerisation, this is a point that cannot be decided without further experiment. Strong sulphuric acid causes polymerisation to take place instantly with formation of a solid substance. It was also found that if hexatriene is placed in a tube full of oxygen over mercury it undergoes oxidation, the volume of gas soon becoming greatly reduced.

The following results are the averages obtained from the examination of the two fractions above referred to, obtained after different intervals of time:

Av. b. p. 77·7—79°.

Density: $d4°/4°$, 0·75190; $d15°/15°$, 0·74229; $d25°/25°$, 0·73444.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
13·75°	2·0402	12·196

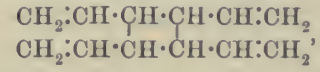
Refractive power:

$d16\cdot2°/4° = 0\cdot74067$

	μ 16·2°.	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$
H_α	1·47819	0·64562	51·650
H_β	1·50272	0·67878	54·302
H_γ	1·51958	0·70155	56·124

Disp. $H\gamma - H\alpha = 4\cdot472$.

It was thought that it would be interesting to determine the magnetic rotation and refraction values of the crude polymerised product left from the distillation of hexatriene, because if it were formed from the hydrocarbon with the production of



$$\begin{array}{l}CH_2{:}CH\cdot CH\cdot CH\cdot CH{:}CH_2\\CH_2{:}CH\cdot CH\cdot CH\cdot CH{:}CH_2\end{array}$$,

this substance would contain no associated double linkings and would therefore give very much lower values than two molecules of hexatriene itself. The following results were obtained:

Polymerised hexatriene distilling above 95°.

Density: d 15°/15° 0·88494; d 25°/25° 0·87920.

Magnetic rotation:

		Mol. Rot.	
t	Sp. Rot.	For C_6H_8.	For $(C_6H_8)_2$.
14°	1·7605	8·836	17·673

Refractive power:

d 16·75°/4° = 0·88295

			$\frac{\mu-1}{d}p$	
	μ16·75°.	$\frac{-1}{d}$	For C_6H_8.	For $(C_6H_8)_2$.
H_α......	1·51569	0·58406	46·725	93·450
H_β......	1·53348	0·60421	48·337	96·674
H_γ......	1·54481	0·61703	49·362	98·724

The following are the results obtained compared with those of hexatriene:

Magnetic rotation:

Rot. of 2 mols. of Hexatriene	24·380
,, ,, polymerised product taken as $(C_6H_8)_2$ ...	17·672
Reduction due to polymerisation ...	6·708

Refractive power:

H_α 2 mols. of Hexatriene	... ...	103·300
,, polymerised product taken as $(C_6H_8)_2$	...	93·449
Reduction due to polymerisation	...	9·851

The magnetic rotation of a polymeride of the above constitution should be about equivalent to that of 2 molecules of diallyl less 4H, thus:

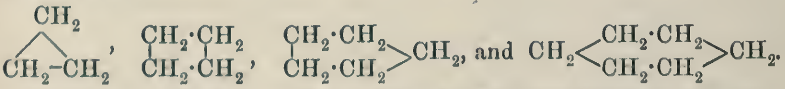
Rot. of 2 mols. diallyl (8·420 × 2) =	16·840
less 4H	1·016
	15·824

Considering the product still contained traces of hexatriene which would raise its rotation (which is about 1·85 too high), it would appear not unlikely that polymerisation takes place in the direction indicated above.

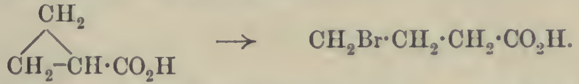
LXXVI.—*The Action of Tribromopropane on the Sodium Derivative of Ethyl Malonate. Part I.*

By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN (Schunck Research Fellow in the University of Manchester).

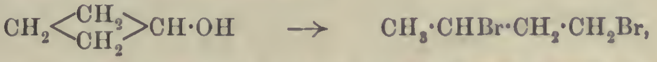
ONE of the most difficult problems in connexion with the chemistry of closed carbon chains is the determination of the relative stability of the rings in the series, *cyclo*propane, *cyclo*butane, *cyclo*pentane, *cyclo*hexane, &c.,



During the discussion of his well known "Spannungs Theorie" (*Ber.*, 1885, 18, 2279), Baeyer expressed the view that the five-carbon *cyclo*pentane ring would be found to be the most stable combination, and that the *cyclo*butane ring would be more stable than the *cyclo*propane ring. Many facts have, however, come to light, especially during the last few years, which seem to indicate that, whilst the *cyclo*butane ring is, on the whole, more stable than the *cyclo*propane ring, the *cyclo*propane ring is, at all events under certain conditions, much more readily produced than the *cyclo*butane ring. It is well known that trimethylenecarboxylic acid suffers disruption when it is treated with hydrobromic acid in the cold,

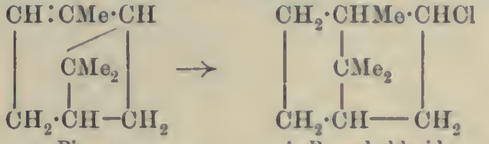


*cyclo*Butanecarboxylic acid is stable to hydrobromic acid, but *cyclo*butanol, on the other hand, is converted into $\alpha\gamma$-dibromobutane when it is treated with hydrobromic acid,

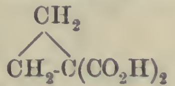


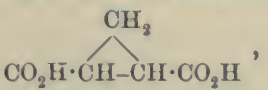
$$CH_2{<}{\scriptstyle CH_2 \atop CH_2}{>}CH\cdot OH \longrightarrow CH_3\cdot CHBr\cdot CH_2\cdot CH_2Br,$$

and the dimethyl*cyclo*butane ring in pinene suffers disruption when the terpene is treated with hydrogen chloride even at – 20° :



Pinene. *iso*Bornyl chloride.

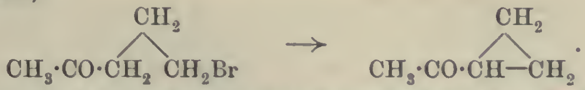
The careful study of the behaviour of a number of derivatives clearly proves that the stability of the *cyclo*propane and *cyclo*butane rings depends to a much greater extent on the nature and position of the groups attached to the ring than to the number of carbon atoms which the ring contains. Thus, for example, whilst *cyclo*propane-1 : 1-dicarboxylic acid,  , is characterised by the ease with which it suffers disruption, the 1 : 2-dicarboxylic acid,



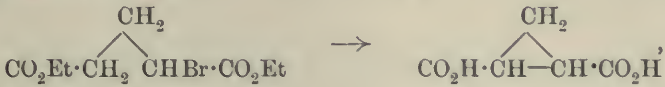
is a substance of quite remarkable stability.

With regard to whether the *cyclo*propane or the *cyclo*butane ring is the more readily produced, the evidence seems to be, in many cases at least, in favour of the *cyclo*propane ring, as may be gathered from the following considerations.

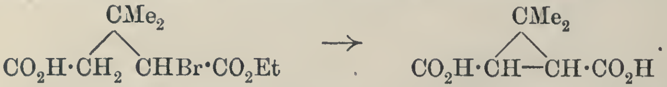
Acetylpropyl bromide yields acetyl*cyclo*propane when it is treated with alkalis,



Alcoholic potash converts ethyl α-bromoglutarate into *cyclo*propane-1 : 2-dicarboxylic acid,

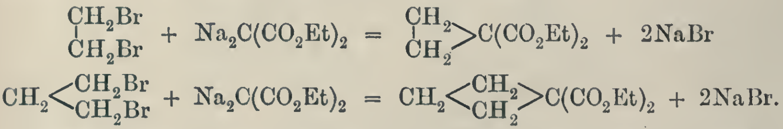


and caronic acid is produced quantitatively when ethyl hydrogen *a*-bromodimethylglutarate is digested with alcoholic potash,



The *cyclo*butane ring does not appear to be formed under conditions analogous to the above.

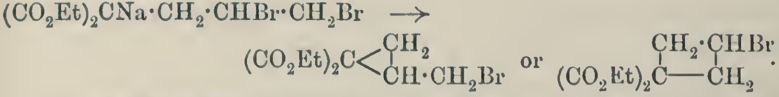
The object of the present investigation was to endeavour to solve the problem of the relative ease of formation of the *cyclo*propane and *cyclo*butane rings experimentally by employing some reaction which offered equal possibilities for the formation of the two rings. It is well known that the sodium derivative of ethyl malonate reacts with ethylene bromide and trimethylene bromide with the formation of *cyclo*propane- and *cyclo*butane-dicarboxylic esters,



$$\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} + Na_2C(CO_2Et)_2 = \begin{matrix}CH_2\\|\\CH_2\end{matrix}>C(CO_2Et)_2 + 2NaBr$$

$$CH_2<\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + Na_2C(CO_2Et)_2 = CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>C(CO_2Et)_2 + 2NaBr.$$

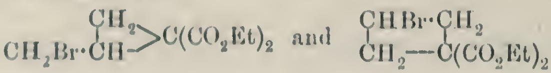
Now tribromopropane, $CH_2Br\cdot CHBr\cdot CH_2Br$, may be said to contain, within its molecule, both ethylene bromide and trimethylene bromide, and therefore, always provided that, of the three bromine atoms, one of those in the *a*-position reacts in the first instance with the sodium derivative of ethyl malonate, there should then be equal chances in the second stage of the reaction for the closing of either the *cyclo*propane or *cyclo*butane ring,



$$(CO_2Et)_2CNa\cdot CH_2\cdot CHBr\cdot CH_2Br \longrightarrow (CO_2Et)_2C<\begin{matrix}CH_2\\|\\CH\cdot CH_2Br\end{matrix} \text{ or } \begin{matrix} & CH_2\cdot CHBr\\ & |\qquad|\\ (CO_2Et)_2C & \!\!-\!\!-\!\!-CH_2\end{matrix}.$$

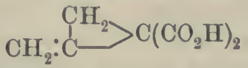
In order to ascertain the relative stability of the *a*- and *β*-bromine atoms, we treated tribromopropane with sodium ethoxide and obtained *β*-bromoallyl ethyl ether, $CH_2{:}CBr\cdot CH_2\cdot OEt$, a decomposition which proves that the *β*-bromine atom reacts less readily than the two others, and this would rather favour the subsequent formation of the *cyclo*butane ring.

The sodium derivative of ethyl malonate was now mixed with tribromopropane when a vigorous reaction took place, and we obtained a bromo-ester, $C_{10}H_{15}O_4Br$, which yielded a dibasic acid, $C_4H_4(CO_2H)_2$, on treatment with alcoholic potash, and this acid was readily decomposed by heat with formation of the correponding monobasic acid, $C_4H_5\cdot CO_2H$. The two formulæ for the bromo-ester which at once suggested themselves were

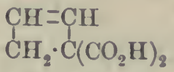


$$\begin{matrix}CH_2\\|\\CH_2Br\cdot CH\end{matrix}>C(CO_2Et)_2 \text{ and } \begin{matrix}CHBr\cdot CH_2\\|\qquad|\\CH_2-C(CO_2Et)_2\end{matrix},$$

and hydrolysis with alcoholic potash with elimination of hydrogen bromide would then lead to formulæ such as



and



for the dibasic acid, formulæ which appeared to agree remarkably well with the observed properties of this acid.* After a long investigation, however, we ultimately discovered that the decomposition of tribromopropane, by the sodium derivative of ethyl malonate, proceeds in a quite unexpected direction, since it is entirely different from that exhibited by ethylene bromide or trimethylene bromide under exactly similar conditions. There can now be no doubt that the bromo-ester, $C_{10}H_{15}O_4Br$, is *ethyl γ-bromoallylmalonate*, $CH_2{:}CBr{\cdot}CH_2{\cdot}CH(CO_2Et)_2$, and the proof of its constitution is as follows.

(*a*) When treated with sodium ethoxide and methyl iodide it yields a methyl derivative, $CH_2{:}CBr{\cdot}CH_2{\cdot}CMe(CO_2Et)_2$, and therefore, since it contains a replaceable hydrogen atom, it cannot be a ring compound, as is represented by the formulæ given above.

(*b*) It is reduced with difficulty, but when its alcoholic solution is added to molten sodium it yields allylmalonic acid,

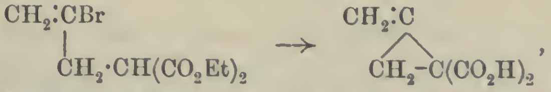
$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H)_2.$$

(*c*) The γ-position of the bromine atom is proved by the fact that the bromo-ester yields *acetonylmalonic acid* when it is treated either with (i) potassium carbonate or (ii) with hydrobromic acid,

$$\text{(i)}\ CH_2{:}CBr{\cdot}CH_2{\cdot}CH(CO_2Et)_2 \longrightarrow CH_2{:}C(OH){\cdot}CH_2{\cdot}CH(CO_2Et)_2 \longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CO_2H)_2$$

$$\text{(ii)}\ CH_2{:}CBr{\cdot}CH_2{\cdot}CH(CO_2Et)_2 \longrightarrow CH_3{\cdot}CBr_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2 \longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CO_2H)_2,$$

and there can be no doubt that the acid thus produced is acetonylmalonic acid, since heat decomposes it with elimination of carbon dioxide and formation of levulinic acid. The properties of the acid, $C_4H_4(CO_2H)_2$, obtained when the bromo-ester is treated with alcoholic potash suggested that it was probably an unsaturated *cyclo*propane derivative produced according to the scheme:



but this assumption was again proved to be incorrect by the discovery that the ester of this acid, when treated with sodium ethoxide and methyl iodide, yields a methyl derivative and therefore contains a replaceable hydrogen atom. The observation was then made that the dibasic acid, $C_4H_4(CO_2H)_2$, and the monobasic acid, $C_4H_5{\cdot}CO_2H$, derived from it by the elimination of carbon dioxide, not only yield abnormal and explosive silver salts of the formulæ

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* Compare Proc., 1906, **22**, 133, where the formula of the bromo-ester is, however, erroneously given as $C_{10}H_{15}O_2Br$ instead of $C_{10}H_{15}O_4Br$.

$$C_4H_4(CO_2Ag)_2,AgOH$$

and $C_4H_5(CO_2Ag),AgOH$ respectively, but also that their aqueous solutions are precipitated by ammoniacal cuprous chloride with the formation of yellow copper derivatives. It is therefore clear that the action of alcoholic potash on the bromo-ester has resulted in the formation of an acetylene derivative, and the constitutional formulæ of the dibasic and monobasic acids must therefore be

$$CH⋮C{\cdot}CH_2{\cdot}CH(CO_2H)_2 \text{ and } CH⋮C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H.$$

We propose the names Δ^{γ}-*butinene-αα-dicarboxylic acid* and Δ^{γ}-*butinene-α-carboxylic acid* for these two acids.

Δ^{γ}-Butinene-αα-dicarboxylic acid is remarkably stable, since it is not reduced when its aqueous solution is boiled with sodium amalgam; on the other hand, the ester is reduced to allylmalonic acid,

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H)_2,$$

when its alcoholic solution is gradually added to molten sodium. Although butinenedicarboxylic acid does not yield an additive compound with bromine, it reacts readily with hydrobromic acid, but the additive compound formed is very easily attacked by moisture with the formation of acetonylmalonic acid, a process which probably takes place thus:

$$CH⋮C{\cdot}CH_2{\cdot}CH(CO_2H)_2 \longrightarrow CH_3{\cdot}CBr_2{\cdot}CH_2{\cdot}CH(CO_2H)_2$$
$$\longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CO_2H)_2.$$

Δ^{γ}-*Butinene-α-carboxylic acid* is also remarkably stable and is not attacked when its aqueous solution is boiled with sodium amalgam, nor could a definite additive product with bromine be isolated.

On the other hand, it yielded *γγ-dibromovaleric acid*,

$$CH_3{\cdot}CBr_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

and *γγ-di-iodovaleric acid*, $CH_3{\cdot}CI_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, when it was treated with hydrobromic and hydriodic acids in the cold and the ester was reduced to allylacetic acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, by treatment with alcohol and sodium.

The methyl derivatives of the above acids, namely,

$$CH⋮C{\cdot}CH_2{\cdot}CMe(CO_2H)_2 \text{ and } CH⋮C{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$$

(Δ^{δ}-*pentinene-ββ-dicarboxylic acid* and Δ^{δ}-*pentinene-β-carboxylic acid*), have been prepared by several processes and carefully investigated; they exhibit properties closely corresponding with those of the parent acids.

The determination of the densities, magnetic rotations, and refractive powers of the new substances described in this communication was undertaken by Sir W. H. Perkin (p. 835), and the bearing of the results on the question of the constitution of these substances is discussed on p. 838.

Ethyl γ-Bromoallylmalonate, $CH_2\!:\!CBr\cdot CH_2\cdot CH(CO_2Et)_2$.

In preparing this ester, sodium (33 grams) is dissolved in absolute alcohol (400 c.c.) and, after cooling, a mixture of tribromopropane (200 grams) and ethyl malonate (228 grams) gradually added.

The reaction takes place with sufficient evolution of heat to bring the alcohol to the boiling point, much sodium bromide is deposited, and, after remaining overnight, the whole is heated on the water-bath for half an hour in order to ensure complete decomposition. Water is then added, the oil extracted with ether, the ethereal solution washed, dried over calcium chloride, evaporated, and the almost colourless residue fractionated under reduced pressure (26 mm.). After a good deal of unchanged ethyl malonate has passed over at about 100—120°, the thermometer rises to about 150°, between which point and 160° a large fraction is obtained and a heavy oil, which is described later (p. 842), (*A*) remains in the distilling flask.

The fraction 150—160° (26 mm.) is then subjected to further fractionation, when an oil is readily obtained which distils constantly at 154° (26 mm.), but, in spite of the constant boiling point, very varying analytical numbers were obtained with different specimens, a fact which is doubtless due to the elimination of some hydrogen bromide during distillation. In one case the following relatively satisfactory results were obtained:

0·1651 gave 0·2480 CO_2 and 0·0735 H_2O. C = 41·0; H = 5·0.
0·2407 „ 0·1650 AgBr. Br = 29·1.
$C_{10}H_{15}O_4Br$ requires C = 43·0; H = 5·5; Br = 28·7 per cent.

Other specimens contained bromine varying between 27·9 and 30 9 per cent. *Ethyl γ-bromoallylmalonate* is a colourless oil with a pungent, unpleasant odour, in which the bromine atom is firmly fixed, since it is only very slowly eliminated when the ester is digested with diethylaniline.

Action of Hydrobromic Acid. Formation of Acetonylmalonic Acid, $CH_3\cdot CO\cdot CH_2\cdot CH(CO_2H)_2$.—The bromo-ester (10 c.c.) was mixed in a sealed tube with five times its weight of aqueous hydrobromic acid (saturated at 0°) and gently warmed, when the ester completely dissolved and, after heating at 100° for half an hour, an oil was observed to have separated on the surface of the acid. The brown liquid was poured into water and extracted three times with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, when a brown, oily acid was obtained which gradually became semi-solid. In contact with porous porcelain the dark oily impurity was rapidly absorbed, and, after crystallising from water, a colourless crystalline acid was obtained which melted at about 143° with decomposition. That this acid was *acetonylmalonic acid* was proved by careful comparison with a specimen of this acid which had been prepared by the process described on p. 826.

Action of Potassium Carbonate on Ethyl γ-Bromoallylmalonate. Formation of Acetonylmalonic Acid.—In studying this decomposition, the bromo-ester (30 grams) was digested with a strong solution of potassium carbonate (90 grams) in a reflux apparatus, when the oil gradually dissolved, but even after sixty hours a small quantity still remained. This was removed by filtration, the aqueous solution was then acidified, and extracted several times with ether.

The ethereal solution was dried over calcium chloride and evaporated, when a crystalline acid was obtained which, after remaining in contact with porous porcelain until quite free from oil, was recrystallised from ethyl acetate :

0·1399 gave 0·2297 CO_2 and 0·0657 H_2O. C = 44·8 ; H = 5·3.

$C_6H_8O_5$ requires C = 45·0 ; H = 5·0 per cent.

This acid melted at about 146° with decomposition, and when mixed with a specimen of acetonylmalonic acid, prepared by the process described on p. 826, the melting point of the mixture was 147—148°.

Reduction to Allylmalonic Acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH(CO_2H)_2$.—In studying this reduction, sodium (25 grams) was heated at 120° in a reflux apparatus by means of an oil-bath, and then the bromo-ester (20 grams) dissolved in alcohol (300 grams) was gradually added through the condenser. When all the sodium had dissolved, the product was mixed with water, evaporated until free from alcohol, acidified, and extracted several times with ether, when a solid acid was obtained which, after crystallising from water, melted at 102° and consisted of *allylmalonic acid*.

0·1684 gave 0·3100 CO_2 and 0·0805 H_2O. C = 50·2 ; H = 5·3.

$C_6H_8O_4$ requires C = 50·0 ; H = 5·6 per cent.

The identity of the acid was further proved by direct comparison with a specimen of allylmalonic acid prepared from ethyl malonate.

Δγ-Butinene-aa-dicarboxylic Acid, $CH{:}C{\cdot}CH_2{\cdot}CH(CO_2H)_2$.

This acid is produced by the hydrolysis of ethyl γ-bromoallylmalonate with alcoholic potash, and the conditions most suitable for its formation seem to be the following.

Ethyl γ-bromoallylmalonate (30 grams) is dissolved in a solution of caustic potash (60 grams) in methyl alcohol (300 c.c.) and heated to boiling for one hour in a reflux apparatus, during which operation much potassium bromide separates. The product is diluted with water and evaporated until free from methyl alcohol; it is then acidified and extracted ten times with ether. After drying over calcium chloride and evaporating, the ethereal solution deposits an oil which, over sulphuric acid in a vacuum desiccator, soon begins to crystallise and ultimately becomes semi-solid. In contact with porous porcelain the oily impurity is gradually absorbed, and the residual acid may be purified by crystallisation from ether.

The yield of pure acid is, however, much improved if the crude acid is converted into its ester, and this, after fractionation, hydrolysed. The crude acid (30 grams) is dissolved in a cold mixture of alcohol (300 c.c.) and sulphuric acid (30 c.c.), and, after remaining overnight, heated for three hours on the water-bath.

The product is mixed with ether, water is then added, and the ethereal solution separated, washed with water and dilute sodium carbonate, dried over calcium chloride, and evaporated. After two distillations, almost the whole of the ester passes over at 129° (22 mm.) as a colourless oil with a pleasant ethereal odour:

0·2095 gave 0·4657 CO_2 and 0·1325 H_2O. C = 60·5; H = 7·1.
$C_{10}H_{14}O_4$ requires C = 60·6; H = 7·1 per cent.

The hydrolysis of *ethyl Δγ-butinene-αα-dicarboxylate* was carried out as follows: sodium (3·5 grams) was dissolved in alcohol (50 c.c.), the solution mixed with water (50 c.c.), and the ester (15 grams) added. After heating on the water-bath for half an hour, the oil had completely dissolved, and the solution was then mixed with water and evaporated until free from alcohol. The residue was acidified, extracted ten times with ether, the ethereal solution dried over calcium chloride and evaporated, when a crystalline solid remained which consisted of the almost pure dibasic acid.

For analysis it was recrystallised from ether:

0·1905 gave 0·3524 CO_2 and 0·0735 H_2O. C = 50·4; H = 4·3.
0·1768 „ 0·3287 CO_2 „ 0·0698 H_2O. C = 50·7; H = 4·3.
$C_6H_6O_4$ requires C = 50·7; H = 4·2 per cent.

Δγ-Butinene-αα-dicarboxylic acid crystallises from ether, in which it is readily soluble, in colourless, glistening plates; it softens at 130° and melts at 139° with vigorous evolution of carbon dioxide and formation of the corresponding monocarboxylic acid.

It is readily soluble in water, alcohol, or acetic acid, but sparingly so in benzene, chloroform, or light petroleum. The determination of the dissociation constant gave $k = 0·2258$.

Salts of Δγ-Butinene-αα-dicarboxylic Acid.—The basicity of the acid was first determined by titration with *N*/10 caustic soda, using phenolphthalein as indicator, when 0·1212 neutralised 16·9 c.c., whereas this amount of a dibasic acid, $C_6H_6O_4$, should neutralise 17·0 c.c.

The *silver* salt, $C_6H_4O_4Ag_2,AgOH$.—When the solution of the acid in water is made slightly alkaline with ammonia and, after warming to 50°, mixed with an excess of silver nitrate, a white, caseous precipitate separates, which is collected, well washed with water, in which it is sparingly soluble, drained on porous porcelain, and dried at 80°. As this salt explodes violently on heating, special precautions had to be taken in analysing it. The silver was determined as chloride by heating with hydrochloric acid and nitric acid in a sealed tube, and in carrying out the carbon and hydrogen determinations the salt was mixed with a long layer of copper oxide:

0·2933 gave 0·1655 CO_2 and 0·0348 H_2O. C = 15·4; H = 0·9.
0·2925 ,, 0·1691 CO_2 ,, 0·0269 H_2O. C = 15·7; H = 1·0.
0·890 ,, 0·7910 AgCl. Ag = 66·7.
0·4432 ,, 0·3967 AgCl. Ag = 67·4.
$C_6H_4O_4Ag_2,AgOH$ requires C = 15·0; H = 1·0; Ag = 67·4 per cent.

Since this silver salt had such an abnormal composition, it seemed at first possible that during preparation addition of water might have taken place with formation of a hydroxy-tribasic acid capable of forming a trisilver salt. In order to investigate this point, a quantity of the silver salt was prepared, dissolved in ammonia, and after precipitating the silver with hydrochloric acid the acid was extracted with ether. The ethereal solution was dried over calcium chloride and evaporated to a small bulk, when almost colourless crystals gradually separated which melted at 139° and consisted of pure Δ^γ-butinene-*aa*-dicarboxylic acid:

0·1807 gave 0·3359 CO_2 and 0·0751 H_2O. C = 50·6; H = 4·2.
$C_6H_6O_4$ requires C = 50·7; H = 4·2 per cent.

The curious composition of the silver salt made it interesting to see whether other salts were abnormal, and the behaviour of a slightly alkaline solution of the ammonium salt was therefore investigated, with the result that the highly characteristic calcium salt was selected for examination.

When calcium chloride is added to the cold slightly alkaline solution of the ammonium salt the liquid remains clear, but warming on the water-bath soon causes the calcium salt to separate as a heavy, sandy powder, which, under the microscope, is seen to consist of nearly square plates. The salt was collected by the aid of the pump and washed well, when, after remaining exposed to the air for three days, it yielded analytical results agreeing fairly well with the formula $C_6H_4O_4Ca,2H_2O$, and therefore this salt is normally constituted:

0·2183 gave 0·2603 CO_2, 0·0691 H_2O, and 0·0600 CaO. C = 32·54; H = 3·5; Ca = 20·0.

$C_6H_4O_4Ca,2H_2O$ requires C = 33·3; H = 3·7; Ca = 18·5 per cent.

The fact that the carbon is rather low and the calcium too high is due to the difficulty experienced in completely freeing the lime from carbon. A determination of the calcium as sulphate was therefore carried out:

0·3156 gave 0·1958 $CaSO_4$. Ca = 18·5.

This salt does not appear to lose water of crystallisation when dried at 100°; it dissolves in dilute hydrochloric acid, and the dibasic acid is obtained in a pure state by extraction with ether.

The ammonium salt of the dibasic acid gives no precipitate with barium chloride even on boiling; lead acetate produces an immediate curdy white precipitate, and copper sulphate gives no precipitate in the cold, but, on boiling, the solution clouds and copper is gradually reduced.

Properties of Δ^{γ}*-Butinene-αα-dicarboxylic Acid.*—When the aqueous solution of the acid is mixed with a solution of cuprous chloride in ammonia a very pale yellow, voluminous precipitate of the copper derivative separates, which becomes deeper yellow and caseous on warming. The acid behaves as an unsaturated acid, since its solution in sodium carbonate reduces permanganate, although not very rapidly. On the other hand, the solution of the acid in chloroform does not decolorise bromine, and all attempts to obtain a dibromo-addition product, by leaving the acid in contact with bromine or bromine vapour, lead only to sticky products from which nothing crystalline could be obtained. The stability of the acid towards sodium amalgam was well shown by the following experiment.

The pure acid (1 gram) was dissolved in sodium carbonate and the boiling solution treated with 100 grams of 3 per cent. sodium amalgam. After cooling and acidifying, ether extracted about 1 gram of a crystalline acid, which, after crystallising from ether, melted at 139° and consisted of the unchanged dibasic acid.

When, however, the ester of butinenedicarboxylic acid (p. 823), dissolved in alcohol, is added to molten sodium under the conditions given in detail in the case of the ester of the monocarboxylic acid (p. 829), it yields a crystalline acid which contains allylmalonic acid, since it is decomposed on distillation with formation of allylacetic acid, the identity of which was proved by conversion into γδ-dibromovaleric acid, $CH_2Br\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO_2H$ (m. p. 58°).

Acetonylmalonic Acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH(CO_2H)_2$.

This acid is formed when Δ^{γ}-butinene-$\alpha\alpha$-dicarboxylic acid is treated with hydrobromic acid. The powdered acid is just covered with fuming aqueous hydrobromic acid (saturated at 0°) and kept in ice and salt, when it gradually dissolves with the evolution of some gas, and after remaining overnight the dark brown solution will be found to have deposited a crystalline substance. This is collected and purified by recrystallisation from dry ether, in which it is rather sparingly soluble and from which it separates in colourless, glistening plates:

0·1831 gave 0·2993 CO_2 and 0·0828 H_2O. $C = 44·6$; $H = 5·1$.

$C_6H_8O_5$ requires $C = 45·0$; $H = 5·0$ per cent.

Acetonylmalonic acid is very soluble in water, and melts at 150° with decomposition into carbon dioxide and levulinic acid.

The basicity of the acid was determined by titration with standard caustic potash solution, when 0·1168 neutralised 0·081 KOH, whereas this amount of a dibasic acid, $C_6H_8O_5$, should neutralise 0·0818 KOH. The *silver* salt was obtained as a white, flocculent precipitate on the addition of silver nitrate to the slightly alkaline solution of the ammonium salt:

0·1689 gave 0·0973 Ag. $Ag = 57·6$.

$C_6H_6O_5Ag_2$ requires $Ag = 57·7$ per cent.

The *semicarbazone* is deposited as a crystalline precipitate when semicarbazide acetate is added to an aqueous solution of the acid. It crystallises from water in stellate groups and melts at about 170° with vigorous decomposition:

0·1645 gave 26·6 c.c. nitrogen at 14° and 773 mm. $N = 19·5$.

$C_7H_{11}O_5N_3$ requires $N = 19·4$ per cent.

The constitution of acetonylmalonic acid is proved by its conversion into levulinic acid and carbon dioxide on heating above its melting point. The dibasic acid was heated at about 180° until the evolution of carbon dioxide had ceased, and the residue dissolved in water and warmed with an aqueous solution of phenylhydrazine and a few drops of acetic acid (E. Fischer, *Annalen*, 1886, **236**, 146), when an oily precipitate separated which soon crystallised.

This hydrazone, after crystallisation from benzene, melted at 108°, and, when mixed with a specimen of the hydrazone of levulinic acid, no alteration in the melting point could be observed.

The semicarbazone of the levulinic acid, obtained by elimination of carbon dioxide from acetonylmalonic acid, separated at once when the aqueous solution was mixed with semicarbazide acetate and crystallised from water in fern-like groups melting at 186—188° with decomposition :

0·2889 gave 58·9 c.c. nitrogen at 13° and 771 mm. N = 24·5.
$C_6H_{11}O_3N_3$ requires N = 24·3 per cent.

As we were unable to find a description of the semicarbazone of levulinic acid, we prepared it in the ordinary way and found that, after crystallisation from water, it melted at about 188° with decomposition. It has been pointed out (pp. 821, 822) that acetonylmalonic acid is also produced when ethyl γ-bromoallylmalonate is treated with hydrobromic acid or digested with potassium carbonate.

Δγ-*Butinene-a-carboxylic Acid*, $CH⋮C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.

This acid is readily obtained by heating Δγ-butinene-*aa*-dicarboxylic acid at 150° until all evolution of carbon dioxide has ceased, and that the decomposition is a quantitative one was proved by the following experiment: 0·32 gram of the dibasic acid yielded 0·23 gram of butinenecarboxylic acid, whereas theoretically 0·22 gram should have been produced. The solid acid, thus obtained, is readily purified by crystallisation from light petroleum, from which it separates in long, satiny needles which resemble benzoic acid :

0·1999 gave 0·4481 CO_2 and 0·1117 H_2O. C = 61·1 ; H = 6·2.
0·1573 ,, 0·3542 CO_2 ,, 0·0903 H_2O. C = 61·3 ; H = 6·3.
$C_5H_6O_2$ requires C = 61·2 ; H = 6·1 per cent.

Δγ-*Butinene-a-carboxylic acid* melts at 57° and distils at 203—204° (766 mm.) ; it is readily soluble in cold water and in most organic solvents. The determination of the dissociation constant gave $k = 0{\cdot}00404$.

Salts of Δγ-*Butinene-a-carboxylic Acid.*—The basicity of the acid was first determined by titration with *N*/10 caustic soda, using phenolphthalein as indicator, when it was found that 0·0626 gram of the acid neutralised 6·4 c.c., whereas this amount of a monobasic acid, $C_5H_6O_2$, should have neutralised 6·38 c.c.

The *silver* salt, $C_5H_5O_2Ag,AgOH$, is somewhat soluble in water, and, in order to prepare it, a rather concentrated solution of the ammonium salt was precipitated with silver nitrate, the gelatinous precipitate was then collected, washed as well as possible, and drained on porous porcelain. The salt explodes vigorously when heated in a test-tube, giving a light, carbonaceous mass which covers the empty part of the tube; the combustion had therefore to be carried out by mixing the substance with a long layer of finely-divided copper oxide. The silver was determined as chloride by heating the salt with nitric acid and hydrochloric acid at 180° for two hours :

0·2570 gave 0·1561 CO_2 and 0·0454 H_2O. C = 16·7; H = 2·0.
0·2334 ,, 0·1671 CO_2 ,, 0·0320 H_2O. C = 19·5; H = 1·5.
0·2863 ,, 0·2536 AgCl. Ag = 66·6.
$C_5H_5O_2Ag,AgOH$ requires C = 18·2; H = 1·9; Ag = 66·5 per cent.

The neutral solution of the ammonium salt gives no precipitate with barium or calcium chlorides or with lead acetate; copper sulphate gives no precipitate in the cold, but, on warming, the solution clouds and the copper is gradually reduced.

Properties of $\Delta\gamma$-Butinene-α-carboxylic Acid.

The aqueous solution of this acid yields, on the addition of ammoniacal cuprous chloride, a very voluminous, yellow, gelatinous precipitate of the copper derivative.

Although unsaturated, butinenecarboxylic acid is not reduced even when its aqueous solution is boiled with sodium amalgam and the solution in chloroform does not decolorise bromine. If, however, the acid is dissolved in dry bromine and the excess of the latter allowed to slowly evaporate over potash in a vacuum desiccator, a viscid, almost colourless oil is obtained which contains 68 per cent. of bromine, whereas the additive compound, $C_5H_6O_2Br_2$, contains 62 per cent.

Oxidation to Succinic Acid.—Like the corresponding dibasic acid, $\Delta\gamma$-butinene-α-carboxylic acid does not reduce permanganate very rapidly, but the oxidation proceeds regularly if the solution in sodium carbonate is agitated with a stirrer and carbon dioxide is passed during the gradual addition of the permanganate. When the colour remains for half an hour, the excess is removed with sodium bisulphite, the whole heated to boiling, filtered, and the filtrate and washings of the manganese precipitate evaporated to a small bulk, acidified, and extracted many times with ether. On evaporation, the ethereal solution deposited a solid acid which, after crystallisation from water, melted at 185° and consisted of pure succinic acid:

0·1787 gave 0·2654 CO_2 and 0·0864 H_2O. C = 40·5; H = 5·3.
$C_4H_6O_4$ requires C = 40·7; H = 5·1 per cent.

γγ-Dibromovaleric Acid, $CH_3{\cdot}CBr_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.

$\Delta\gamma$-Butinene-α-carboxylic acid dissolves in aqueous hydrobromic acid, saturated at 0°, with much evolution of heat, and, in order to avoid rise of temperature, the acid (1 gram) was gradually added to the hydrobromic acid (5 grams) and the whole carefully cooled with ice and salt. After remaining overnight, water precipitated an oil which soon solidified. The crystals were collected, drained on porous porcelain, and crystallised from light petroleum, from which γγ-dibromovaleric acid separated in colourless plates melting at 52—53°:

0·2042 gave 0·1705 CO_2 and 0·0520 H_2O. C = 22·7 ; H = 2·8.
0·1644 „ 0·2379 AgBr. Br = 61·5.
$C_5H_8O_2Br_2$ requires C = 23·0 ; H = 3·0 ; Br = 61·5 per cent.

γγ-Di-iodovaleric acid, $CH_3·CI_2·CH_2·CH_2·CO_2H$, is prepared in a similar way by gradually adding Δγ-butinene-α-carboxylic acid (2·5 grams) to 10 grams of a solution of hydrogen iodide in acetic acid (saturated at 0°), the whole being carefully cooled in ice and salt. After twenty-four hours, the solution was poured into water, the yellow solid collected by the aid of the pump, washed with dilute sodium bisulphite to remove iodine, and purified by crystallisation from light petroleum, from which γγ-di-iodovaleric acid separates in colourless needles melting at 90°:

0·2182 gave 0·1431 CO_2 and 0·0439 H_2O. C = 17·8 ; H = 2·2.
0·0991 „ 0·1321 AgBr. I = 72·0
$C_5H_8O_2I_2$ requires C = 16·9 ; H = 2·2 ; I = 71·7 per cent.

Ethyl Δγ-Butinene-α-carboxylate, $CH⋮C·CH_2·CH_2·CO_2Et$.

In order to prepare this ester, the pure acid (7 grams) is dissolved in a cold mixture of alcohol (60 grams) and sulphuric acid (7 grams). After seven days, water is added, the oily ester extracted with ether, the ethereal solution washed with water and dilute sodium carbonate, dried over calcium chloride, evaporated, and the residual oil distilled.

0·1914 gave 0·4665 CO_2 and 0·1317 H_2O. C = 66·6 ; H = 7·9.
$C_7H_{10}O_2$ requires C = 66·5 ; H = 7·7 per cent.

Ethyl Δγ-butinene-α-carboxylate distils at 160—161° (765 mm.) and has a pungent and rather unpleasant odour.

Reduction of Ethyl Δγ-Butinene-α-carboxylate to Allylacetic Acid.

In carrying out this reduction the ester (20 grams) was dissolved in alcohol (200 grams) and gradually added through a long condenser to sodium (25 grams) kept at 120° by means of an oil-bath. Alcohol was then gradually added until the sodium had completely dissolved, and, after the addition of water, the solution was evaporated on the water-bath until free from alcohol. The liquid was then acidified and extracted with ether, the ethereal solution dried over calcium chloride and evaporated, and the residual oil distilled, when almost the whole quantity passed over at 188° (759 mm.):

0·1716 gave 0·3742 CO_2 and 0·1241 H_2O ; C = 59·4 ; H = 8·1.
$C_5H_8O_2$ requires C = 60·0 ; H = 8·0 per cent.

That this oil was *allylacetic acid* was proved by the fact that, when exposed to bromine vapour, it was gradually converted into a solid substance which, after crystallising from light petroleum, melted at 58° and gave the following results on analysis:

0·1541 gave 0·1294 CO_2 and 0·0406 H_2O. C = 22·8 ; H = 2·9.
0·2116 ,, 0·3070 AgBr. Br = 61·7.
$C_5H_8O_2Br_2$ requires C = 23·0 ; H = 3·0 ; Br = 61·5 per cent.

This substance is obviously *γδ-dibromovaleric acid*,

$$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

the melting point of which, prepared from allylacetic acid, is stated by Messerschmidt (*Annalen*, 1881, **208**, 100) to be 58°.

Δ^δ-*Pentinene-ββ-dicarboxylic Acid*, $CH{:}C{\cdot}CH_2{\cdot}CMe(CO_2H)_2$.

This acid has been prepared by three different processes.

I. *By the Action of Tribromopropane on the Sodium Derivative of Ethyl Methylmalonate.*—In carrying out this synthesis, sodium (33 grams) dissolved in alcohol (400 c.c.) was mixed with tribromopropane (200 grams) and ethyl methylmalonate (248 grams), when a vigorous action set in and the temperature rapidly rose to the boiling point.

The product was treated in the way already described in detail in the case of ethyl malonate (p. 821), and yielded an oil almost the whole of which (with the exception of unchanged ethyl methylmalonate) distilled at 145—147° (13 mm.) and did not leave an oil of high boiling point as was the case when ethyl malonate was employed.

The oil which distilled at 145—147° is *ethyl methyl-γ-bromoallylmalonate*, $CH_2{:}CBr{\cdot}CH_2{\cdot}CMe(CO_2Et)_2$, as the following analysis shows:

0·2266 gave 0·3583 CO_2 and 0·1095 H_2O ; C = 43·1 ; H = 5·4.
0·1631 ,, 0·1069 AgBr. Br = 27·8.
$C_{11}H_{17}O_4Br$ requires C = 45·0 ; H = 5·8 ; Br = 27·3 per cent.

When treated with alcoholic potash, under the conditions described on p. 822, this bromo-ester yielded a colourless, crystalline acid which separated from a mixture of ether and light petroleum in colourless plates:

0·2052 gave 0·4039 CO_2 and 0·0894 H_2O. C = 53·7 ; H = 4·8.
$C_7H_8O_4$ requires C = 53·8 ; H = 5·1 per cent.

Δ^δ-*Pentinene-ββ-dicarboxylic acid* melts at 134° with decomposition into carbon dioxide and the corresponding monobasic acid.

It is readily soluble in water, ether, alcohol, chloroform, or benzene, but sparingly so in light petroleum. Its aqueous solution gives, with ammoniacal cuprous chloride, a very pale yellow, voluminous precipitate of the copper derivative, which, on warming, becomes deeper yellow and caseous. The acid is not reduced when its aqueous solution is boiled with sodium amalgam and, in spite of several attempts, no addition product with bromine could be isolated.

The oxidation of Δ^{δ}-pentinene-$\beta\beta$-dicarboxylic acid, carried out exactly as described on p. 828, yielded methylsuccinic acid which, after crystallising from light petroleum, melted at 112°, and the identity of which was proved by mixing with a sample of methylsuccinic acid prepared by another process, when no alteration in melting point could be observed. The acid was also analysed:

0·1512 gave 0·2516 CO_2 and 0·0813 H_2O. C = 45·3; H = 6·0.

$C_5H_8O_4$ requires C = 45·4; H = 6·1 per cent.

The *silver* salt of Δ^{δ}-pentinene-$\beta\beta$-dicarboxylic acid,

$C_7H_6O_4Ag_2,AgOH$,

was obtained as a white precipitate when silver nitrate was added to a slightly alkaline solution of the ammonium salt. Since it was not so explosive as the silver salt of Δ^{γ}-butinene-$\alpha\alpha$-dicarboxylic acid (p. 824) it was found possible to analyse it in the usual manner, but the results obtained were rather low:

0·1799 gave 0·1144 Ag. Ag = 63·5.
0·2971 ,, 0·1879 Ag. Ag = 63·2.

$C_7H_6O_4Ag_2,AgOH$ requires Ag = 65·4 per cent.

Ethyl Δ^{δ}-*Pentinene*-$\beta\beta$-*dicarboxylate*, $CH\vdots C\cdot CH_2\cdot CMe(CO_2Et)_2$.

This ester was prepared by leaving the pure dibasic acid (20 grams) in contact with alcohol (100 c.c.) and sulphuric acid (10 c.c.) for twenty-four hours and then heating on the water bath for two hours. It is a colourless oil which distils at 122—123° (15 mm.) and possesses a pungent but not disagreeable odour:

0·1473 gave 0·3362 CO_2 and 0·1003 H_2O. C = 62·3; H = 7·5.

$C_{11}H_{16}O_4$ requires C = 62·3; H = 7·5 per cent.

When the ester is shaken with an ammoniacal solution of cuprous chloride, an almost colourless, flocculent precipitate of the copper derivative rapidly separates.

II. *By the Action of Methyl Iodide on the Sodium Derivative of Ethyl* γ-*Bromoallylmalonate*.—This process was carried out as follows. Ethyl γ-bromoallylmalonate (29 grams) was mixed with a cold solution of sodium (2·4 grams) in alcohol (35 c.c.) and then methyl iodide (20 grams) added, the temperature being kept below 40° by cooling with water. After remaining overnight, water was added, the oil extracted with ether and fractionated, when almost the whole quantity distilled at 145—150° (18 mm.). This was hydrolysed with alcoholic potash in the usual manner, and, after mixing with water and evaporating until free from alcohol, the solution was acidified and extracted with ether. The ethereal solution was dried over calcium chloride and evaporated, when a solid acid was obtained which separated from light petroleum in plates, melted at 134° with decomposition, and consisted of pure Δ^{δ}-*pentinene-ββ-dicarboxylic acid*:

0·1314 gave 0·2582 CO_2 and 0·0615 H_2O. C = 53·6; H = 5·2.

$C_7H_8O_4$ requires C = 53·8; H = 5·1 per cent.

III. *By the Action of Methyl Iodide on the Sodium Derivative of Ethyl* Δ^{γ}-*Butinene-aa-dicarboxylate.*—In carrying out this method of preparation, sodium (0·6 gram) was dissolved in alcohol, mixed with ethyl Δ^{γ}-butinene-*aa*-dicarboxylate (5 grams) and methyl iodide (3·5 grams), and heated on the water-bath for two hours. The product was mixed with water, the ester extracted with ether, and, after removing the ether by evaporation, the residue was hydrolysed by digesting with a slight excess of alcoholic potash. The solution was diluted with water, evaporated until free from alcohol, acidified, and extracted with ether, when a solid acid was obtained which crystallised from a mixture of ether and light petroleum in plates, melted at 134°, and was found by direct comparison to be identical with the Δ^{δ}-pentinene-ββ-dicarboxylic acid described above.

Δ^{δ}-*Pentinene-β-carboxylic Acid*, $CH⋮C\cdot CH_2\cdot CHMe\cdot CO_2H$.

When Δ^{δ}-pentinene-ββ-dicarboxylic acid is heated in a distilling flask under the ordinary pressure, carbon dioxide is eliminated and an oil passes over at 200—210° which, after redistillation, boils constantly at 207—208° (768 mm.).

0·2666 gave 0·6228 CO_2 and 0·1670 H_2O. C = 63·7; H = 7·0.

$C_6H_8O_2$ requires C = 64·3; H = 7·1 per cent.

Δ^{δ}-*Pentinene-β-carboxylic acid* is a viscous, colourless oil which has an unpleasant odour somewhat resembling that of valeric acid.

It is rather sparingly soluble in water and its solution in sodium carbonate rapidly decolorises permanganate. The basicity of the acid was first determined by titration with standard caustic potash solution, when 0·3088 gram neutralised 0·151 KOH, whereas this amount of a monobasic acid, $C_6H_8O_2$, should neutralise 0·153 KOH.

The *silver* salt, $C_6H_7O_2Ag,AgOH$, is obtained as a white, flocculent precipitate when silver nitrate is added to a slightly alkaline solution of the ammonium salt. It was collected by the aid of the pump, washed well and dried over sulphuric acid in a vacuum desiccator:

0·2271 gave 0·1429 Ag. Ag = 62·9.
0·2796 ,, 0·1767 Ag. Ag = 63·1.

$C_6H_7O_2Ag,AgOH$ requires Ag = 62·8 per cent.

Ethyl Δ^{δ}-*Pentinene-β-carboxylate*, $CH⋮C\cdot CH_2\cdot CHMe\cdot CO_2Et$.—In preparing this ester, the pure acid (15 grams) was mixed with a cold solution of sulphuric acid (10 c.c.) in alcohol (80 c.c.) and allowed to stand for ten days at the ordinary temperature. Water was then added, the oil extracted with ether, the ethereal solution washed well with dilute sodium carbonate, dried over calcium chloride, evaporated, and the ester twice fractionated:

0·1759 gave 0·4400 CO_2 and 0·1342 H_2O. C = 68·2; H = 8·4.

$C_8H_{12}O_2$ requires C = 68·6; H = 8·6 per cent.

Ethyl Δ^{β}-pentinene-β-carboxylate has a pleasant ethereal odour and distils at 165—167° (757 mm.).

Action of Sodium Ethoxide on Tribromopropane. Formation of β-Bromoallyl Ethyl Ether, $CH_2{:}CBr{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$.

When tribromopropane (100 grams) is added to a cold solution of sodium (24·5 grams) in alcohol (300 grams), a rapid rise of temperature takes place and much sodium bromide separates. After boiling on the water-bath for half an hour, the product was diluted with water, extracted several times with ether, the ethereal solution dried over calcium chloride, and the ether very slowly distilled off. On fractionating the oil, it was separated into two portions boiling at 80—130° and 130—135°. The latter is *β-bromoallyl ethyl ether* and identical with the substance which Henry (*Ber.*, 1872, **5**, 188) prepared from ethyl dibromohydrin, $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$, by the action of caustic soda:

0·2317 gave 0·3094 CO_2 and 0·1169 H_2O. C = 36·4; H = 5·6.
0·1964 ,, 0·2203 AgBr. Br = 48·0.

C_5H_9OBr requires C = 36·3; H = 5·4; Br = 48·4 per cent.

The fraction 80—130° probably contained Δ^{β}-propinene ethyl ether, $CH{:}C{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$, since it yielded a silver derivative when treated with ammoniacal silver nitrate, but it was not further investigated.

Preparation of Propiolic Acid, $CH{:}C{\cdot}CO_2H$, *and Ethyl Propiolate,* $CH{:}C{\cdot}CO_2Et$.

Since Δ^{γ}-butinene-α-carboxylic acid, $CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, is closely allied to propiolic acid, it was thought necessary to prove this relationship by a careful comparison of their physical properties and especially of the magnetic rotations of the acids and their esters. Furthermore, considerable quantities of propiolic acid were required for other investigations and it was therefore important to work out, as carefully as possible, the best method for its preparation. After many comparative experiments, the following process, which is a modification of that devised by Bandrowski (*Ber.*, 1880, **13**, 2340; 1882, **15**, 2701) and Baeyer (*Ber.*, 1885, 18, 677 and 2209), was adopted as the most satisfactory.

Dibromosuccinic acid (50 grams) is dissolved in as little hot alcohol as possible, allowed to cool, and then treated with strong alcoholic potash (KOH = 55 grams), the latter being added in four portions, the whole well agitated, and the temperature kept below 40° during the addition. A caseous precipitate separates at first, but this soon becomes crystalline and, after heating on the water-bath for one hour, the product is filtered by the aid of the pump, the precipitate washed twice with alcohol and dried at about 40°.

The colourless, crystalline mass (potassium acetylenedicarboxylate and potassium bromide) from three such operations is dissolved in as little water as possible, mixed with cold 30 per cent. sulphuric acid (40 grams H_2SO_4), and, after remaining overnight, the precipitate is collected,* dissolved in hot water (350 c.c.), and heated in a reflux apparatus for one hour on the water-bath and then for one hour to boiling. The solution is then cooled, acidified, saturated with ammonium sulphate, and extracted fifteen times with washed ether, the ethereal solution is dried over calcium chloride, evaporated, and the propiolic acid purified by distillation. The purity of the acid prepared in this way was controlled by analysis:

0·1521 gave 0·2850 CO_2 and 0·0411 H_2O. C = 51·1; H = 3·0.
$C_3H_2O_2$ requires C = 51·4; H = 2·9 per cent.

Propiolic acid distils at 83—84° (50 mm.) and solidifies to a crystalline mass which melts at about 9°; the yield obtained from 100 grams of dibromosuccinic acid was 18—20 grams. It is a very irritating liquid which blisters the skin much in the same way as formic acid does. In order to prepare ethyl propiolate, it is not necessary to employ sealed tubes as recommended by Baeyer (*loc. cit.*, p. 688).

The acid (20 grams) is dissolved in alcohol (60 c.c.) and sulphuric acid (6 grams)† and allowed to stand for two days, water is then added, the ester extracted with ether, the ethereal solution washed with dilute sodium carbonate, dried over calcium chloride and fractionated:

0·1319 gave 0·2945 CO_2 and 0·0749 H_2O. C = 60·8; H = 6·4.
$C_5H_6O_2$ requires C = 61·2; H = 6·1 per cent.

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* The filtrate is mixed with dilute sulphuric acid (10 grams H_2SO_4) and, if a further precipitate separates, this is collected and decomposed by heating with water and, in this way, a further small quantity of propiolic acid may sometimes be obtained.

† If larger quantities of sulphuric acid are employed and the solution is heated, esters of higher boiling point are apt to be produced which have not been further investigated.

Ethyl propiolate, $CH\vdots C\cdot CO_2Et$, distils, as stated by Baeyer, at 119° (745 mm.) and its vapour has a very irritating action on the eyes and skin.

Densities, Magnetic Rotations, and Refractive Powers of Ethyl Δ^{γ}-Butinene-aa-dicarboxylate, Ethyl Δ^{γ}-Butinene-a-carboxylate, Ethyl Δ^{δ}-Pentinene-ββ-dicarboxylate, Ethyl Δ^{δ}-Pentinene-β-carboxylate, Propiolic Acid, and Ethyl Propiolate.

The magnetic rotations and refractive powers of the above substances were determined by Sir W. H. Perkin, with the following results.

Ethyl Δ^{γ}-Butinene-aa-dicarboxylate.

The first specimen of this ester examined was prepared by digesting the acid with alcohol and sulphuric acid in the usual way. It distilled at 129° under 22 mm. pressure.

Density :

d 4°/4° = 1·0541 ; d 15°/15° = 1·0444 ; d 25°/25° = 1·0367.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
15·15°	1·1143	11·737

Refractive power :

d 15·9°/4° = 1·04175.

μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α……1·44253	0·42479	84·108
β……1·45176	0·43366	85·864
γ……1·45700	0·43868	86·860

Dispersion, $\gamma - a = 2{\cdot}752$.

Since these results did not agree quite satisfactorily with those obtained in the case of the corresponding monocarboxylic ester (p. 836), a second specimen of the ester was prepared from very carefully purified dibasic acid by treatment with sulphuric acid and alcohol in the cold. It distilled at the same temperature as before and gave density and magnetic rotation values agreeing closely with those obtained in the case of the first specimen.

Density :

d 10°/10° = 1·0492 ; d 15°/15° = 1·0449 ; d 20°/20° = 1·0410.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
15·9°	1·1139	11·733

Ethyl Δ^{γ}-Butinene-α-carboxylate.

The specimen examined distilled at 160—161° (765 mm.).

Density :

$d\ 4°/4° = 0·96848$; $d\ 15°/15° = 0·95835$; $d\ 25°/25° = 0·95002$.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
15·3°	1·1126	8·129

Refractive power :

$d\ 16·7°/4° = 0·95585$.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1·42673	0·44644	56·251
β	1·43516	0·45525	57·362
γ	1·44001	0·46003	58·002

Dispersion, $\gamma - \alpha = 1·751$.

Ethyl Δ^{δ}-Pentinene-ββ-dicarboxylate.

The specimen examined distilled at 122—123° (15 mm.).

Density :

$d\ 4°/4° = 1·04203$; $d\ 15°/15° = 1·03188$; $d\ 20°/20° = 1·02799$; $d\ 25°/25° = 1·02421$.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
16·6°	1·0457	11·949.

Refractive power :

$d\ 17°/4° = 1·02913$.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1·43718	0·42481	90·059
β	1·44565	0·43303	91·803
γ	1·45066	0·43791	92·836

Dispersion, $\gamma - \alpha = 2·777$.

Ethyl Δ^{δ}-Pentinene-β-carboxylate.

This ester distilled at 165—167° (757 mm.).

Density :

$d\ 4°/4° = 0·95424$; $d\ 15°/15° = 0·94404$; $d\ 20°/20° = 0·93989$; $d\ 25°/25° = 0·93602$.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
16·75°	1·0944	9·030

Refractive power :

d 17°/4° = 0·94128.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α......	1·42654	0·45314	63·440
β......	1·43486	0·46198	64·677
γ......	1·43991	0·46735	65·429

Dispersion, $\gamma - \alpha = 1·989$.

Propiolic Acid.

The specimen examined distilled at 83—84° (50 mm.).

Density :

d 4°/4° = 1·1499 ; d 15°/15° = 1·1387 ; d 25°/25° = 1·1301.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
15·3°	1·2415	4·241

Refractive power :

d 15°/4° = 1·13780.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α......	1·43146	0·37921	26·545
β......	1·44293	0·38929	27·250
γ......	1·44623	0·39218	27·452

Dispersion, $\gamma - \alpha = 0·907$.

Ethyl Propiolate.

This ester distilled at 119° (745 mm.).

Density :

d 4°/4° = 0·9788 ; d 15°/15° = 0·9676 ; d 25°/25° = 0·9583.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
15·3°	1·1199	6·311.

Refractive power :

$$d\ 15^\circ/4^\circ = 0{\cdot}96676.$$

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1·41133	0·42577	41·725
β	1·42065	0·43542	42·671
γ	1·42611	0·44108	42·226

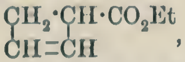
Dispersion, $\gamma - \alpha = 0{\cdot}501$.

The consideration of the results obtained in the determination of the magnetic rotation and refractive power of the substances described in this paper, and which contain the grouping CH⁝C·CH·, was rendered very difficult owing to the want of sufficient evidence as to the value of the acetylenic linking. The only acetylene derivative which had been examined was dipropargyl, $CH{⁝}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{⁝}CH$, the magnetic rotation of which was found to be 10·435. If this be compared with the value for diallyl, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$ (8·420), it is seen that the change from two ethylenic linkings to two acetylenic linkings in the same position is 2·015. Again, the effect of converting the corresponding saturated substance into diallyl is easily calculated by subtracting the magnetic rotation of hexane (6·646) from that of diallyl (8·420), when we obtained 1·774 as the rise in rotation due to the two double linkings, or 0·887 * for each.

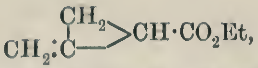
These considerations seemed to indicate that the rise in rotation, due to converting the group $\cdot CH_2{\cdot}CH_2\cdot$ into ·C⁝C·, was rather more than twice that which is produced when $\cdot CH_2{\cdot}CH_2\cdot$ is converted into ·CH:CH·. The rotation of ethyl Δγ-butinene-α-carboxylate was therefore calculated in the following way :

	Mol. rot.
Ethyl *n*-valerate	7·500
Acetylenic linking	1·905
Calculated rotation	9·405

and, since the value actually found was 8·129, the inference was drawn that this ester could not contain an acetylenic linking and must therefore be an unsaturated closed chain compound possessing either of the formulæ,



$$\begin{array}{l}CH_2{\cdot}CH{\cdot}CO_2Et\\CH{=}CH\end{array}\ ,$$



$$CH_2{:}C\!\!\begin{array}{c}CH_2\\ \end{array}\!\!>CH{\cdot}CO_2Et,$$

or some formula closely allied to these, and the observed magnetic rotation was in excellent accord with this assumption (compare Proc., 1906, 22, 133).

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* Owing, no doubt, to the fact that diallyl contains *two* double linkings, this number is rather high. The usual value for the conversion of $\cdot CH_2{\cdot}CH_2\cdot$ into ·CH:CH· deduced from a large number of cases is about 0·720.

During the course of this investigation, facts gradually came to light which pointed strongly in favour of the acetylenic constitution of the substances described in this paper, and it therefore became important to determine the magnetic rotation of acetylene derivatives other than dipropargyl with a view to ascertaining whether this isolated case might not possibly be abnormal. A very pure specimen of propiolic acid, $CH\vdots C\cdot CO_2H$, was accordingly prepared and examined and the results compared with the magnetic rotation of the corresponding saturated substance :

	Mol. rot.
Propiolic acid	4·241
Propionic acid	3·462
Difference	0·779

with the surprising result that the rise in rotation in this case was found to be almost exactly that which is produced when a saturated substance is converted into the corresponding unsaturated substance containing an ethylenic linking. In other words, the rise of rotation was only half that which had been observed in connexion with an acetylenic linking in dipropargyl. It will doubtless be found that the high value of the two acetylenic linkings in dipropargyl is due to the influence which the two groups exert on one another.*

A comparison of the formulæ of ethyl propiolate, $CH\vdots C\cdot CO_2Et$, and ethyl Δ^γ-butinene-α-carboxylate, $CH\vdots C\cdot CH_2\cdot CH_2\cdot CO_2Et$, shows that these substances are closely related, and if the difference for the change from propionic acid to propiolic acid is applied, we find that the calculated rotation of ethyl Δ^γ-butinene-α-carboxylate

Ethyl *n*-valerate	7·500
Acetylenic linking	0·779
Calculated rotation	8·279

agrees well with that actually found (8·129), especially when we note that the acetylenic linking is in a different position with respect to the carboxyethyl-group in the two cases.

Similarly, it may be shown that the magnetic rotation values of ethyl Δ^δ-pentinene-β-carboxylate and the other substances, described in this paper as derivatives of acetylene, are in all cases in harmony with this view of their constitution. It is also interesting to observe that the values obtained for the refractive power of propiolic acid and its ester point in the same direction as the magnetic rotation values, and indicate that the rise in refraction, due to the introduction of the acetylenic linking, is not much greater than that produced by introducing an ethylenic linking.

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* While this communication was in the press we found two papers by Griner (*Ann. Chim. Phys.*, 1892 [vi], **26**, 347) and Faworsky (*J. pr. Chem.*, 1891, [ii], **44**, 233) in which it is shown that dipropargyl, prepared in the usual manner from diallyl, is a mixture of hydrocarbons. If, as seems to be the case, ordinary dipropargyl contains the hydrocarbon, $CH_3\cdot C\vdots C\cdot C\vdots C\cdot CH_3$, the presence of the two associated treble linkings may account for the high value found for the magnetic rotation.

Thus the refractive power of propiolic acid for Hα is 26·545, whereas the value calculated for an acid, $C_3H_2O_2$, containing an ethylenic linking is 26·1.

The authors wish to express their thanks to the Research Fund Committee of the Society for a grant in aid of the expenses of this investigation.

THE SCHUNCK LABORATORY,
THE VICTORIA UNIVERSITY OF MANCHESTER.

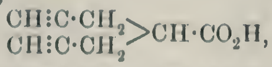
LXXVII.—*The Action of Tribromopropane on the Sodium Derivative of Ethyl Malonate. Part II. Formation of* $\Delta^{\alpha\zeta}$*-Heptadi-inene-δ-carboxylic Acid* (ψ-m-*Toluic Acid*), $(CH{:}C\cdot CH_2)_2C(CO_2H)_2$.

By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN (Schunck Research Fellow in the University of Manchester).

THE principal product of the action of tribromopropane on the sodium derivative of ethyl malonate is *ethyl γ-bromoallylmalonate,* a detailed account of which is given in the preceding communication, and it is there stated that besides this substance, another bromo-ester (b. p. 191°/11 mm.) is always produced in considerable quantities. Investigation has shown that this bromo-ester is *ethyl γγ-dibromodiallylmalonate,* produced according to the equation

$$2CH_2Br\cdot CHBr\cdot CH_2Br + 4NaCH(CO_2Et)_2 = (CH_2{:}CBr\cdot CH_2)_2C(CO_2Et)_2 + 3CH_2(CO_2Et)_2 + 4NaBr.$$

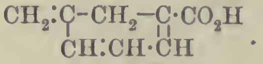
When this ester is digested with alcoholic potash, it is decomposed with elimination of hydrogen bromide and formation of $\Delta^{\alpha\zeta}$*-heptadi-inene-δ-carboxylic acid,*



$$\begin{matrix} CH{:}C\cdot CH_2 \\ CH{:}C\cdot CH_2 \end{matrix}\!\!>CH\cdot CO_2H,$$

which crystallises in prisms and melts at 47°. This interesting acid, like Δ^{γ}-butinene-α-carboxylic acid, $CH{:}C\cdot CH_2\cdot CH_2\cdot CO_2H$ (p. 827), of which it is a derivative, evidently contains acetylene linkings, since it yields a copper derivative when its aqueous solution is mixed with ammoniacal cuprous chloride and the silver salt has an abnormal composition, the analytical numbers lying between those required by the formulæ $C_8H_7O_2Ag,AgOH$ and $2AgOH$.

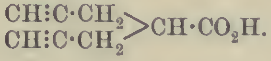
The interest which attaches to this acid is due to the extraordinary ease with which it is converted into the isomeric *m*-toluic acid, and this remarkable intramolecular change led us in the first instance (Proc., 1906, 22, 134) to name the acid "*ψ*-m-*toluic acid*" and to assign to it the constitution



$$\begin{array}{l} CH_2{:}C{-}CH_2{-}C{\cdot}CO_2H \\ \quad\;\; CH{:}CH{\cdot}CH \end{array}$$

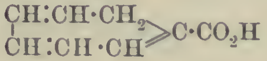
The conversion into *m*-toluic acid takes place when the acid is simply boiled with water or when it is treated in the cold with hydrobromic acid, but heat alone does not bring about this change.

The discovery that the acid yields a copper derivative and especially the study of the values obtained in the determination of the magnetic rotation of ethyl *ψ*-*m*-toluate (p. 845) caused us to discard the above formula, and there can now no longer be any doubt that the constitution of the acid is represented by the formula



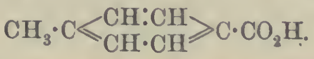
$$\begin{array}{l} CH{\vdots}C{\cdot}CH_2 \\ CH{\vdots}C{\cdot}CH_2 \end{array}\!\!>CH{\cdot}CO_2H.$$

ψ-*m*-Toluic acid is therefore somewhat closely allied to *iso*phenylacetic acid,*



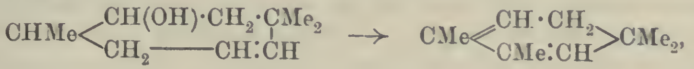
$$\begin{array}{l} CH{:}CH{\cdot}CH_2 \\ CH{:}CH{\cdot}CH \end{array}\!\!\geqslant C{\cdot}CO_2H$$

(Buchner, *Ber.*, 1898, 31, 987; Braren and Buchner, *Ber.*, 1891, 34, 987), and it is worthy of note that this acid when heated at 100° with a solution of hydrogen bromide in acetic acid is converted by intramolecular change into a derivative of *p*-toluic acid,



$$CH_3{\cdot}C\leqslant\begin{array}{l} CH{:}CH \\ CH{\cdot}CH \end{array}\!\!\geqslant C{\cdot}CO_2H.$$

The only other somewhat similar cases which we have been able to find are the formation of tetramethyldihydrobenzene (euterpene) from dihydroeucarveol by the action first of phosphorus pentachloride and then of quinoline (Baeyer, *Ber.*, 1898, 31, 2077),



$$CHMe<\begin{array}{l} CH(OH){\cdot}CH_2{\cdot}CMe_2 \\ CH_2{-\!\!-\!\!-}CH{:}CH \end{array} \longrightarrow CMe\leqslant\begin{array}{l} CH{\cdot}CH_2 \\ CMe{:}CH \end{array}\!\!>CMe_2,$$

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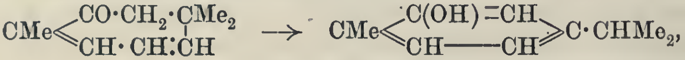
* For some time we were of opinion that *ψ*-*m*-toluic acid was identical with *a*-*iso*phenylacetic acid, and we are greatly indebted to Prof. Buchner for sending us a specimen of this valuable acid which enabled us to decide against the identity.

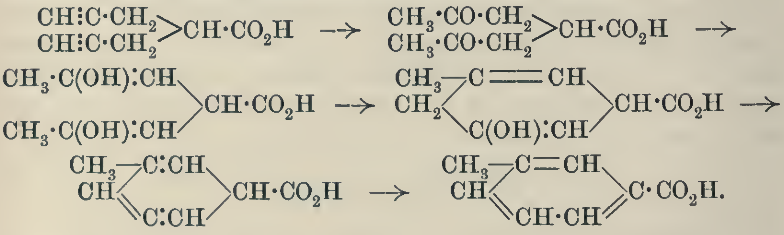
and the case of eucarvone, which when heated to boiling for an hour is quantitatively converted into carvacrol,



$$\mathrm{CMe}\lessgtr\begin{matrix}\mathrm{CO\cdot CH_2\cdot CMe_2}\\ \mathrm{CH\cdot CH{:}CH}\end{matrix} \rightarrow \mathrm{CMe}\lessgtr\begin{matrix}\mathrm{C(OH){=}CH}\\ \mathrm{CH{-\!-\!-}CH}\end{matrix}\gtrless\mathrm{C\cdot CHMe_2},$$

and when treated in the cold with phosphorus pentachloride yields 2-chlorocymene (Klages and Kraith, *Ber.*, 1899, **32**, 2558).

In endeavouring to find an explanation of the remarkable ease with which *ψ-m*-toluic acid is converted into *m*-toluic acid, it should be borne in mind that the intramolecular change takes place rapidly when the acid is boiled with water or dilute acids, but is not brought about by heat alone (p. 843). If we assume that the water, which appears to be essential to the transformation, is added to the acetylenic linkings in *ψ-m*-toluic acid (in the way so frequently observed in other cases) and is then eliminated again, we obtain the following comparatively simple explanation of the conversion into *m*-toluic acid:



Ethyl γγ-Dibromodiallylmalonate, $(\mathrm{CH_2{:}CBr{\cdot}CH_2})_2\mathrm{C(CO_2Et)_2}$, *and its Conversion into Δ^{αζ}-Heptadi-inene-δ-carboxylic Acid* (*ψ*-m-*Toluic Acid*), $(\mathrm{CH{:}C{\cdot}CH_2})_2\mathrm{C(CO_2H)_2}$.

When tribromopropane reacts with the sodium derivative of ethyl malonate, under the conditions described in the preceding communication, an oil (*A*) of high boiling point is always obtained in considerable quantity (compare p. 821). This was twice fractionated under 11 mm. pressure, when almost the whole quantity distilled at about 191°:

0·2296 gave 0·3313 CO_2 and 0·0971 H_2O. C = 39·3; H = 4·7.
0·2434 „ 0·2310 AgBr. Br = 40·3.
$C_{13}H_{18}O_4Br_2$ requires C = 39·2; H = 4·5; Br = 40·2 per cent.

Ethyl γγ-dibromodiallylmalonate is a viscid, heavy oil, possessing a rather unpleasant odour, and is very slowly attacked by boiling with dilute sulphuric acid or with potassium carbonate. Its conversion into *ψ-m*-toluic acid was effected as follows.

The dibromo-ester (20 grams) was mixed with a strong solution of caustic potash (25 grams) in methyl alcohol, when a large quantity of sodium bromide immediately separated, and, after boiling for three hours on the water-bath, the solution was diluted with water and evaporated until free from alcohol. After mixing with powdered ice, hydrochloric acid was added until the solution just reacted with congo-paper, and the oily precipitate was rapidly extracted three times with ether. The ethereal solution was dried over calcium chloride and evaporated, when an oil remained which, over sulphuric acid in a vacuum desiccator, gradually crystallised. The crystals were left in contact with porous porcelain until quite free from oil, and then recrystallised several times from light petroleum (b. p. 60—70°). Three different preparations were analysed:

0·1027 gave 0·2639 CO_2 and 0·0533 H_2O. C = 70·1; H = 5·8.
0·1837 „ 0·4670 CO_2 „ 0·0998 H_2O. C = 69·3; H = 6·0.
0·1459 „ 0·3726 CO_2 „ 0·0782 H_2O. C = 69·6; H = 6·0.
$C_8H_8O_2$ requires C = 70·5; H = 5·9 per cent.

$\Delta^{\alpha\zeta}$-*Heptadi-inene-δ-carboxylic acid* (*ψ-m*-toluic acid) melts at 47° and is unaltered by heating at 150° for half an hour, since the acid solidified again on cooling and melted at the same temperature as before. It is readily soluble in most organic solvents, but rather sparingly so in cold water or light petroleum. When its solution in light petroleum is allowed to evaporate spontaneously, the acid separates in magnificent, glistening prisms. The solution of the sodium salt decolorises permanganate instantly, but the acid is not reduced when it is treated with a large excess of sodium amalgam in the cold. The aqueous solution of the acid gives with ammoniacal cuprous chloride an immediate dense yellow precipitate of the copper derivative. The determination of the dissociation constant of *ψ-m*-toluic acid gave $k = 0·01307$, which is considerably higher than that of *m*-toluic acid ($k = 0·00514$).

*Salts of ψ-*m*-Toluic Acid.*—The basicity of the acid was determined by titration with standard caustic potash solution, when 0·1299 neutralised 0·072 KOH, whereas this amount of a monobasic acid, $C_8H_8O_2$, should neutralise 0·0727 KOH. The neutral solution of the ammonium salt gives no precipitate with barium, calcium, zinc, or magnesium chlorides; copper sulphate gives no precipitate in the cold, but, on warming, a deep blue copper salt separates.

The *silver* salt, like the corresponding silver salt of Δ^{γ}-butinene-*α*-carboxylic acid (p. 827), has an abnormal composition. It was prepared by adding excess of silver nitrate to a cold, slightly alkaline solution of the ammonium salt, and obtained in the form of a voluminous, white precipitate, which was collected by the aid of the pump, washed with warm water, alcohol, and ether, and dried over sulphuric acid in a vacuum desiccator. Although only slowly affected by light, this salt is highly explosive, and the silver had therefore to be determined as chloride by heating the salt with hydrochloric and nitric acids in a sealed tube. Two different preparations gave the following results:

0·3615 gave 0·3035 AgCl. Ag = 63·1.
0·1704 „ 0·1464 AgCl. Ag = 64·6.
$C_8H_7O_2Ag,AgOH$ requires Ag = 58·7; $C_8H_7O_2Ag,2AgOH$ requires Ag = 65·7 per cent.

These analyses indicate that the salt, prepared in the above manner, is a mixture of varying quantities of the two silver salts, $C_8H_7O_2Ag,AgOH$ and $C_8H_7O_2Ag,2AgOH$.

Ethyl ψ-m-*toluate*, $(CH⋮C\cdot CH_2)_2CH\cdot CO_2Et$, was prepared by adding the pure acid (20 grams) to a cold mixture of alcohol (100 c.c.) and sulphuric acid (10 c.c.), and, after remaining for a week, the solution was mixed with water and the ester extracted with ether. The ethereal solution was washed with water and dilute sodium carbonate, the ether evaporated, and the ester distilled under reduced pressure:

0·1250 gave 0·3334 CO_2 and 0·0821 H_2O. C = 72·7; H = 7·3.
$C_{10}H_{12}O_2$ requires C = 73·1; H = 7·3 per cent.

Ethyl ψ-m-*toluate* is a colourless oil which possesses a pleasant ethereal odour and distils at 113° (20 mm.). On hydrolysis it yields ψ-*m*-toluic acid, showing that no molecular change had taken place during its preparation.

The density, magnetic rotation, and refractive power of ethyl ψ-*m*-toluate and of a very pure specimen of ethyl *m*-toluate were determined by Sir W. H. Perkin with the following results:

Ethyl ψ-m-*Toluate.*

Density:

d 10°/10° = 1·0052; d 15°/15° = 1·0009; d 20°/20° = 0·9971.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
15·4°	1·3031	11·876

Refractive power:

d 15·3°/4° = 0·99993.

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1·45795	0·45798	75·109
β	1·46806	0·46809	76·767
γ	1·47397	0·47401	77·737

Dispersion, $\gamma - \alpha$ = 2·628.

Ethyl m-*Toluate*, b. p. 231° (750 mm.).

Density :

d 10°/10° = 1·0374 ; d 15°/15° = 1·0336 ; d 20°/20 = 1·0301.

Magnetic rotation :

t.	Sp. rot.	Mol. rot.
15·5°	1·6746	14·773

Refractive power :

d 14·5°/4° = 1·03313.

	μ.	$\frac{\mu-1}{d}$	$\frac{\mu-1}{d}p$.
α	1·50468	0·48850	80·114
β	1·52085	0·50415	82·680
γ	1·53124	0·51420	84·329

Dispersion, $\gamma - \alpha = 4·215$.

These values are interesting in several ways. In the first place they show clearly the close relationship existing between ethyl ψ-*m*-toluate and ethyl Δ^{γ}-butinene-α-carboxylate.

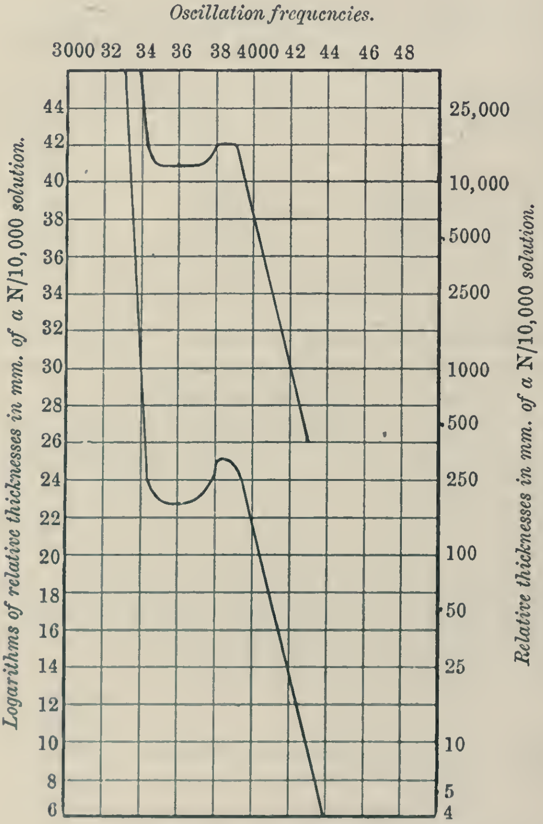
Ethyl Δ^{γ}-butinene-α-carboxylate, $CH⋮C·CH_2·CH_2·CO_2Et$, may be regarded as acetic ester in which hydrogen has been replaced by the group $CH⋮C·CH_2·$, and the value for this group may therefore be calculated by subtracting the rotation of ethyl acetate (4·462) from that of ethyl Δ^{γ}-butinene-α-carboxylate (8·129) and amounts to 3·667. Since, then, ethyl ψ-*m*-toluate, $(CH⋮C·CH_2)_2CH·CO_2Et$, is acetic ester in which two atoms of hydrogen have been replaced by two $CH⋮C·CH_2·$ groups, it is clear that the magnetic rotation of this ester may be calculated in the following way :

	Mol. rot.
Acetic ester	4·462
$2CH⋮C·CH_2·$ replacing 2H	7·334
Ethyl ψ-*m*-toluate (calc.)..........	11·796

This number agrees well with that actually found (11·876), and this fact is strong evidence in favour of the views of the constitutions of Δ^{γ}-butinene-α-carboxylic acid and ψ-*m*-toluic acid which have been adopted in these communications. Another point of interest in connexion with the relationship between ψ-*m*-toluic and *m*-toluic acids is the remarkable rise in magnetic rotation and also in refractive power and dispersion which accompanies the intramolecular change from the ψ-acid to the benzene derivative, as is well seen from the following comparison :

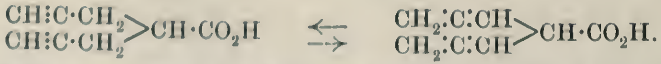
	Mol. rot.	Refraction.	Dispersion.
ψ-*m*-Toluic ester	11·876	75·109	2·628
m-Toluic ester	14·773	80·114	4·215

Mr. E. C. C. Baly kindly undertook to determine the ultra-violet absorption spectra of ψ-*m*-toluic acid and *m*-toluic acid, and the absorption curves of these substances are shown in the accompanying figure.



Upper curve: ψ-m-*Toluic acid.*
Lower curve: m-*Toluic acid.*

Mr. Baly adds the following comment. "ψ-*m*-Toluic acid shows a small absorption band which is undoubted evidence of some form of tautomerism, and this may, possibly, be due to the mobility of two hydrogen atoms of the two ·CH_2· groups, and may be expressed thus:



$$\left.\begin{array}{l}CH⋮C\cdot CH_2\\CH⋮C\cdot CH_2\end{array}\right>CH\cdot CO_2H \quad \overset{\longleftarrow}{\longrightarrow} \quad \left.\begin{array}{l}CH_2⁚C⁚CH\\CH_2⁚C⁚CH\end{array}\right>CH\cdot CO_2H.$$

There is a very striking difference between the curves of ψ-*m*-toluic and *m*-toluic acids, for, although they are of the same shape, the benzenoid absorption occurs at a hundred times the dilution at which the absorption of the ψ-acid occurs. This is clear evidence that ψ-*m*-toluic acid is not benzenoid in character, since simple benzene derivatives do not exhibit their absorption spectra at such great concentrations (*N*/10)."

Conversion of $\Delta^{a\zeta}$*-Heptadi-inene-δ-carboxylic Acid* (ψ-*m*-Toluic Acid) *into* m-*Toluic Acid.*

This remarkable intramolecular change takes place readily under the following conditions.

(a) *By Boiling with Water.*—When ψ-*m*-toluic acid is boiled with water for two hours it completely dissolves and, on cooling, a crystalline acid separates which melts at 110—111° and consists of pure m-*toluic acid*.

$$0{\cdot}0944 \text{ gave } 0{\cdot}244\ CO_2 \text{ and } 0{\cdot}052\ H_2O. \quad C = 70{\cdot}5,\ H = 6{\cdot}1.$$
$$C_8H_8O_2 \text{ requires } C = 70{\cdot}5;\ H = 5{\cdot}9 \text{ per cent.}$$

The same result is obtained when the acid is digested with dilute hydrochloric or sulphuric acids.

(b) *By the Action of Hydrobromic Acid in the Cold.*—In carrying out this experiment, ψ-*m*-toluic acid (1 gram) was dissolved in a cold solution of hydrogen bromide in acetic acid (saturated at 0°, 5 grams), and, after standing overnight, the solution was allowed to evaporate over solid potash in a vacuum desiccator, when an almost colourless, crystalline residue remained which, after crystallisation from light petroleum, melted at 110° and consisted, as direct comparison showed, of pure *m*-toluic acid.

(c) *By the Action of Phosphorus Pentachloride.*—This experiment, made with the object of preparing the amide of ψ-*m*-toluic acid, resulted in the formation of the amide of *m*-toluic acid. ψ-*m*-Toluic acid (6 grams) was mixed with phosphorus pentachloride (10 grams) and, when the reaction had subsided, the liquid was warmed until the pentachloride had completely dissolved. The product was cooled and then added, drop by drop, to concentrated aqueous ammonia surrounded by ice. A good deal of a dark tarry mass separated, this was filtered off, and the filtrate, on standing, deposited crystals of an amide which separated from ether in colourless needles and melted at 93°:

$$0{\cdot}1959 \text{ gave } 16{\cdot}2 \text{ c.c. nitrogen at } 12{\cdot}5 \text{ and } 758 \text{ mm.} \quad N = 9{\cdot}7.$$
$$C_8H_9O_2N \text{ requires } N = 9{\cdot}3 \text{ per cent.}$$

That this substance was the amide of *m*-toluic acid and not of ψ-*m*-toluic acid was proved by hydrolysis with alcoholic potash, when it yielded pure *m*-toluic acid of melting point 110°. Moreover, Remsen and Reid (*Amer. Chem. J.*, 1899, 21, 290) state that the amide of *m*-toluic acid melts at 94°.

THE SCHUNCK LABORATORY,
THE VICTORIA UNIVERSITY OF MANCHESTER.

LXXVIII.—*The Action of Tribromopropane on the Sodium Derivative of Ethyl Acetoacetate.*

By THOMAS EDWARD GARDNER and WILLIAM HENRY PERKIN, jun.

WHEN tribromopropane is digested in alcoholic solution with the sodium derivative of ethyl acetoacetate, decomposition takes place readily, and the principal product of the action is *ethyl γ-bromoallylacetoacetate* (b. p. 121° under 8 mm.):

$$CH_2Br{\cdot}CHBr{\cdot}CH_2Br + 2COMe{\cdot}CHNa{\cdot}CO_2Et = \\ CH_2{:}CBr{\cdot}CH_2{\cdot}CH(COMe)CO_2Et + COMe{\cdot}CH_2{\cdot}CO_2Et + 2NaBr.$$

Hydrolysis with alcoholic potash converts ethyl γ-bromoallylacetoacetate into *Δ^{γ}-butinene-α-carboxylic acid*, $CH{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, but when digested with dilute sulphuric acid it gradually undergoes ketonic hydrolysis with formation of *γ-bromoallylacetone* (b. p. 83° under 8 mm.):

$$CH_2{:}CBr{\cdot}CH_2{\cdot}CH(COMe)CO_2Et + H_2O = \\ CH_2{:}CBr{\cdot}CH_2{\cdot}CH_2{\cdot}COMe + CO_2 + Et{\cdot}OH.$$

γ-Bromoallylacetone yields an oxime and a semicarbazone, and when reduced with alcohol and sodium is converted into *2-hydroxy-5-hexene* (methylcrotonylcarbinol), $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH)Me$.

When the bromo-ketone is digested with alcoholic potash it is decomposed with elimination of hydrogen bromide and formation of *methyl Δ^{γ}-butinene ketone*, $CH{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, a colourless oil distilling at 149° (749 mm.), which yields a crystalline oxime and semicarbazone and shows the behaviour of an acetylene derivative, since it gives a yellow precipitate of the copper derivative when its aqueous solution is mixed with ammoniacal cuprous chloride.

The sodium derivative of ethyl methylacetoacetate reacts readily with tribromopropane, and the *ethyl methyl-γ-bromoallylacetoacetate*, $CH_2{:}CBr{\cdot}CH_2{\cdot}CMe(COMe)CO_2Et$, produced, when hydrolysed by alcoholic potash, yields *Δ^{δ}-pentinene-β carboxylic acid*,

$$CH{\vdots}C{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H.$$

In the preceding communication it was shown that one of the products of the action of tribromopropane on the sodium derivative of ethyl malonate is ethyl γγ-dibromodiallylmalonate,

$$(CH_2{:}CBr{\cdot}CH_2)_2C(CO_2Et)_2,$$

and that this substance, on hydrolysis with alcoholic potash, yields $\Delta^{\alpha\zeta}$-heptadi-inene-δ-carboxylic acid (*ψ-m*-toluic acid),

$$(CH{\vdots}C{\cdot}CH_2)_2CH{\cdot}CO_2H.$$

The analogous substance, *ethyl γγ-dibromodiallylacetoacetate*,

$$(CH_2{:}CBr{\cdot}CH_2)_2C(COMe)CO_2Et,$$

is produced during the action of tribromopropane on the sodium derivative of ethyl acetoacetate, and is also hydrolysed by alcoholic potash with formation of *ψ-m*-toluic acid.

Ethyl γ-Bromoallylacetoacetate, $CH_2{:}CBr{\cdot}CH_2{\cdot}CH(COMe){\cdot}CO_2Et$.

In preparing this substance, sodium (23 grams) was dissolved in alcohol (300 c.c.) and when quite cold mixed with ethyl acetoacetate (130 grams) and tribromopropane (145 grams). Reaction commenced in the cold, and, after heating for three hours on the water-bath, water was added, the oil extracted with ether, the ethereal solution washed well, dried over calcium chloride, evaporated, and the residual oil repeatedly fractionated under a pressure of 8 mm. It was thus separated into three portions, namely, unchanged ethyl acetoacetate, an oil boiling at 120—121°, and an oil (*C*) which distilled approximately at 175—180° and which is further described on p. 854.

The oil distilling at 120—121° (8 mm.) is *ethyl γ-bromoallylacetoacetate*:

0·2555 gave 0·4020 CO_2 and 0·1215 H_2O. $C = 42{\cdot}9$; $H = 5{\cdot}3$.
0·2578 „ 0·1983 AgBr. $Br = 32{\cdot}7$.

$C_9H_{13}O_3Br$ requires $C = 43{\cdot}3$; $H = 5{\cdot}2$; $Br = 32{\cdot}1$ per cent.

Ethyl γ-bromoallylacetoacetate is a colourless oil of unpleasant odour which has the specific gravity d 10°/10° = 1·3620; d 15°/15° = 1·3569; d 20°/20° = 1·3522. It is a very stable substance, since it is apparently unchanged by boiling with diethylaniline, and even quinoline at the boiling point seems to attack it only very slowly.

When this ester is digested with alcoholic potash, separation of potassium bromide occurs, and the product, after evaporation with water, acidifying, and extracting with ether, yields an acid of melting point 53°, which consists of almost pure *Δ^{γ}-butinene-α-carboxylic acid*, since a mixture of equal quantities of this acid and of the acid of this constitution described in the previous communication (p. 827) melted at 55—57°.

γ-Bromoallylacetone, $CH_2{:}CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

This ketone is produced when ethyl γ-bromoallylacetoacetate is digested with dilute sulphuric acid. The crude bromo-ester, distilling at 120—130° (8 mm.) in quantities of 100 grams, was digested with 20 per cent. sulphuric acid (400 c.c.) for several hours, cooled, and extracted three times with ether. After drying over calcium chloride and evaporating, the residue was separated into γ-bromoallylacetone, distilling at 83° (8 mm.), and unchanged ethyl γ-bromoallylacetoacetate, which latter was again heated with dilute sulphuric acid, and in this way a very good yield of the bromo-ketone was ultimately obtained:

0·2366 gave 0·3520 CO_2 and 0·1120 H_2O. C = 40·6; H = 5·3.
0·3120 „ 0·3315 AgBr. Br = 45·2.
C_6H_9OBr requires C = 40·7; H = 5·1; Br = 45·2 per cent.

γ-Bromoallylacetone distils at 83° (8 mm.), and, when quite pure, at about 195° (757 mm.) with little decomposition.

The *oxime*, $CH_2{:}CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH$, was prepared as follows.

Sodium (2·3 grams) was dissolved in methyl alcohol and mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (7 grams), and, after filtering from the precipitated sodium chloride, the bromo-ketone (12 grams) was added to the filtrate. The solution was allowed to stand for twenty-four hours, diluted with water, and the oxime extracted with ether; the ethereal solution was washed, dried over calcium chloride and evaporated, and the residue rapidly distilled under reduced pressure:

0·2371 gave 16 c.c. nitrogen at 19° and 762 mm. N = 7·8.
$C_6H_{10}ONBr$ requires N = 7·3 per cent.

γ-Bromoallylacetoxime is a colourless oil which distils at 118—120° under 12 mm. pressure.

γ-Bromoallylacetone semicarbazone,
$CH_2{:}CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$.
—When the bromo-ketone (1·8 grams) is mixed with a concentrated aqueous solution of semicarbazide hydrochloride (1·2 grams) and sodium acetate (3 grams) and vigorously shaken on the machine, the crystalline semicarbazone soon commences to separate. After several hours, the crystals were collected at the pump, washed first with water, then with alcohol, and purified by recrystallisation from alcohol, when the semicarbazone was obtained in glistening plates melting at 150° without decomposition:

0·2200 gave 35 c.c. nitrogen at 15° and 756 mm. N = 18·5.
$C_7H_{12}ON_3Br$ requires N = 17·7 per cent.

Reduction of γ-Bromoallylacetone to 2-Hydroxy-5-hexene (methylcrotonylcarbinol), $CH_2\colon CH\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_3$.—When a solution of the bromo-ketone (20 grams) in alcohol (50 grams) is gradually added to sodium (30 grams), heated in a reflux apparatus at 120° by means of an oil-bath, a vigorous reaction takes place with separation of sodium bromide, and when this has slackened alcohol is gradually added until the whole of the sodium has dissolved. The product is mixed with water, extracted several times with ether, the ethereal solution washed with water, dried over potassium carbonate, and evaporated, when an oil remains which distils at 140° (759 mm.):

0·1412 gave 0·3726 CO_2 and 0·1550 H_2O. C = 72·0; H = 12·2.

$C_6H_{12}O$ requires C = 72·0; H = 12·0 per cent.

Methylcrotonylcarbinol had already been prepared by Crow (*Annalen*, 1880, 201, 42) from allylacetone by reduction with sodium amalgam and the boiling point observed by that author was 139°.

When this alcohol was oxidised with chromic acid mixture, using an excess of 25 per cent., an oil was obtained which contained unchanged alcohol, but, after purification by conversion into the semicarbazone and regeneration by dilute hydrochloric acid, it distilled at 128° (749 mm.) and consisted of pure *allylacetone*:

0·1285 gave 0·3464 CO_2 and 0·1204 H_2O. C = 73·5; H = 10·4.

$C_6H_{10}O$ requires C = 73·5; H = 10·2 per cent.

The density and magnetic rotation of γ-bromoallylacetone were determined by Sir W. H. Perkin, with the following results:

Density:

d 10°/10° = 1·38989; *d* 15°/15° = 1·38439; *d* 20°/20° = 1·37934.

Magnetic rotation:

t.	Sp. rot.	Mol. rot.
17·2°	1·4018	9·973

Methyl Δγ-Butinene Ketone, $CH\colon C\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$.

In preparing this ketone, γ-bromoallylacetone (60 grams) was mixed with a hot solution of caustic potash (60 grams) in methyl alcohol (200 grams) and the mixture heated on the water-bath for three hours, when decomposition took place readily with separation of potassium bromide and the liquid became very dark-coloured.

The product was mixed with water and the ketone extracted several times with ether, the ethereal solution was washed with water, dried over calcium chloride, evaporated, and the residual crude ketone purified by distillation under reduced pressure:

0·1311 gave 0·3595 CO_2 and 0·1010 H_2O. C = 74·8; H = 8·5.
C_6H_8O requires C = 75·0; H = 8·3 per cent.

Methyl Δγ-butinene ketone distils at 149° (749 mm.) and has a characteristic odour. It readily decolorises permanganate, gives a voluminous, yellow, copper derivative when its aqueous solution is mixed with ammoniacal cuprous chloride, and yields crystalline derivatives with sodium hydrogen sulphite, phenylhydrazine, hydroxylamine, and semicarbazide. It was unfortunate that, owing to the formation of substances of high boiling point during the above method of preparation, the yield of ketone was always very unsatisfactory.

Methyl Δγ-Butinene ketoxime, $CH\vdots C\cdot CH_2\cdot CH_2\cdot CMe\colon N\cdot OH$, was prepared by adding the ketone (5 grams) to hydroxylamine hydrochloride (3·5 grams) and caustic potash (10 grams) dissolved in a little water, sufficient methyl alcohol being added to produce a clear solution.

After twenty-four hours, the product was rendered acid by the addition of hydrochloric acid, extracted with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, when a colourless oil was obtained which, over sulphuric acid in a vacuum, gradually solidified. The crystals were drained on porous porcelain and crystallised from water, from which the oxime separated in colourless plates of melting point 48—49°:

0·175 gave 19·2 c.c. nitrogen at 16° and 768 mm. N = 12·9.
C_6H_9ON requires N = 12·6 per cent.

Methyl Δγ-butinene ketone semicarbazone separates rapidly when the ketone is shaken with an excess of a solution of semicarbazide acetate. The crystalline precipitate was collected by the aid of the pump, washed with water and cold alcohol, and purified by recrystallisation from dilute alcohol, from which the semicarbazone separates as a glistening, crystalline mass and melts at 135—136° without decomposition:

0·2269 gave 52 c.c. nitrogen at 16° and 765 mm. N = 27·4.
$C_7H_{11}ON_3$ requires N = 27·4 per cent.

The density, magnetic rotation, and refractive power of methyl Δγ-butinene ketone were determined by Sir W. H. Perkin with the following results:

Density:

d 4°/4° = 0·91956; d 15°/15° = 0·91005; d 25°/25° = 0·90245.

Magnetic rotation

t.	Sp. rot.	Mol. rot.
14°	1·2267	7·179

Refractive power:

$$d\ 12{\cdot}5^\circ/4^\circ = 0{\cdot}91174.$$

	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
α	1·43693	0·47923	46·006
β	1·44601	0·48918	46·961
γ	1·45152	0·49522	47·541

Dispersion, $\gamma - \alpha = 1{\cdot}535$.

The values obtained for the magnetic rotation of methyl Δ^γ-butinene ketone are interesting because they confirm the close relationship existing between this ketone and Δ^γ-butinene-α-carboxylic acid and its ester. The effect produced by converting an ester into the corresponding ketone may be estimated thus:

	Mol. rot.
Ethyl propionate, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$	6·477
Methyl propyl ketone, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$	5·499
Difference	0·978

and this is practically the same as the difference (0·950) between the magnetic rotations of ethyl Δ^γ-butinene-α-carboxylate,

$$CH⋮C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$$

(8·129), and methyl Δ^γ-butinene ketone, $CH⋮C{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ (7·179), a proof that these compounds are analogously constituted.

Ethyl Methyl-γ-bromoallylacetoacetate, $CH_2{:}CBr{\cdot}CH_2{\cdot}CMe(COMe){\cdot}CO_2Et$.

In preparing this substance, sodium (23 grams) was dissolved in alcohol (300 c.c.) and, when quite cold, mixed with ethyl methylacetoacetate (144 grams) and tribromopropane (140 grams), care being taken that the temperature did not rise above 40° during the operation.

The reaction commenced at once and, after heating on the water-bath for three hours, the product was isolated and purified by distillation in the usual manner (p. 849) and found to boil at about 138° (26 mm.):

0·2500 gave 0·4183 CO_2 and 0·1305 H_2O. C = 45·6; H = 5·8.
0·3222 „ 0·2293 AgBr. Br = 30·3.
$C_{10}H_{15}O_3Br$ requires C = 45·6; H = 5·7; Br = 30·4 per cent.

When *ethyl methyl-γ-bromoallylacetoacetate* was hydrolysed with alcoholic potash it yielded an acid which distilled at 207—208° and gave the following results on analysis:

0·1574 gave 0·3678 CO_2 and 0·1039 H_2O. C = 63·7; H = 7·3.
$C_6H_8O_2$ requires C = 64·3; H = 7·1 per cent.

There can be no doubt that this acid is identical with Δ^{δ}-*pentinene-a-carboxylic acid*, $CH⋮C·CH_2·CHMe·CO_2H$, the preparation and properties of which are described in detail on p. 832.

Ethyl γγ-Dibromodiallylacetoacetate, $(CH_2:CBr·CH_2)_2C(COMe)·CO_2Et$, *and its Conversion into $\Delta^{\alpha\zeta}$-Heptadi-inene-δ-carboxylic Acid*, (*ψ-m*-Toluic Acid), $(CH⋮C·CH_2)_2CH·CO_2H$.

When the product of the action of tribromopropane on the sodium derivative of ethyl acetoacetate is fractionated, a considerable quantity of an oil of high boiling point is obtained (*C.* p. 849) which distils at about 175—180° (8 mm.) with slight decomposition. Although the analytical results were rather low ($Br = 38$; whereas $C_{12}H_{16}O_3Br$ requires 43·4 per cent.), there can be no doubt that this substance is *ethyl γγ-dibromodiallylacetoacetate* and corresponds with ethyl γγ-dibromodiallylmalonate which is obtained (p. 842) when tribromopropane reacts with the sodium derivative of ethyl malonate. This is clearly proved by the behaviour of the dibromo-ester on treatment with alcoholic potash.

Ethyl γγ-dibromodiallylacetoacetate was digested with excess of alcoholic potash and the product evaporated with water until free from alcohol, cooled to 0°, carefully acidified with hydrochloric acid, and repeatedly extracted with ether. On evaporation, the ethereal solution deposited a viscid syrup and, since this showed no signs of crystallising, it was converted into the ester by means of alcohol and sulphuric acid and the portion distilling at 90—100° (10 mm.) again hydrolysed. The syrupy acid now gradually solidified and, after draining on porous porcelain, it was recrystallised from light petroleum, when colourless crystals were obtained which melted at 47—48° and consisted of pure *ψ*-m-*toluic acid*:

0·2088 gave 0·5400 CO_2 and 0·1153 H_2O. $C = 70·6$; $H = 6·1$.

$C_8H_8O_2$ requires $C = 70·5$; $H = 5·9$ per cent.

The identity of this acid with *ψ-m*-toluic acid (p. 843) was proved by mixing equal quantities of the two preparations, when no alteration in melting point could be observed.

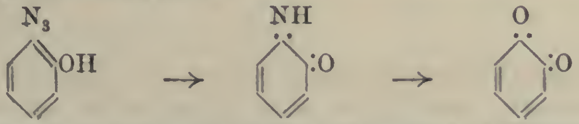
THE SCHUNCK LABORATORY,
THE VICTORIA UNIVERSITY OF MANCHESTER.

LXXIX.—*Aromatic Azoimides. Part I. Parahydroxyphenylazoimide.*

By **Martin Onslow Forster** and **Hans Eduard Fierz.**

In view of the indifference displayed by phenylazoimide towards alcoholic potash, the remarkable facility with which camphorylazoimide is resolved into iminocamphor and nitrogen by minute quantities of this agent (Trans., 1905, 87, 826) suggests a fundamental difference in structure which we believe is best explained by regarding the camphoryl derivative as capable of acting in the enolic form, $C_8H_{14}<\begin{array}{l}C\cdot N_3\\ \|\\ C\cdot OH\end{array}$, in which hydrogen might be expected to migrate readily. Supporting this suggestion, a more recent observation should be noted, namely, the relative stability of the oxime, $C_8H_{14}<\begin{array}{l}CH\cdot N_3\\ |\\ C:NOH\end{array}$, which is not altered by cold, alcoholic potash; moreover, whilst the transparent and colourless crystals of camphorylazoimide quickly become opaque and pink in daylight, a specimen of the oxime has now been exposed during 12 months without undergoing any noticeable change.

From this standpoint, a study of the hydroxyphenylazoimides, particularly the ortho-derivative, seemed attractive, analogy with the enolic modification of camphorylazoimide suggesting the possibility of proceeding to *o*-benzoquinone

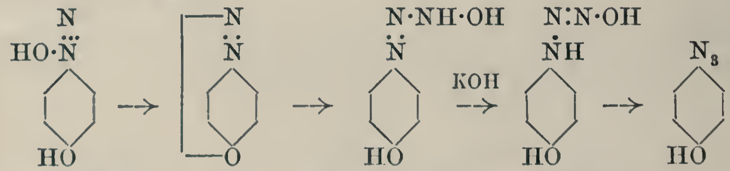


with perhaps less uncertainty than by the method of Willstätter and Pfannenstiel (*Ber.*, 1904, 37, 4744).

Since Griess discovered phenylazoimide in 1866, a considerable number of aromatic azoimides have been described in which hydrogen is replaced by halogens, and by the carboxyl, cyano-, amino-, nitro-, triazo-, and sulphonic groups. Hydroxy-derivatives appear to have escaped attention, however, owing perhaps to various difficulties in dealing with diazophenols, and with the object of gaining experience in the manipulation of hydroxyphenylazoimides before attacking the meta- and ortho-derivatives, we have studied the preparation and properties of the para-compound.

In selecting a method for preparing the substance, it was recognised that the original process for obtaining an aromatic azoimide was inapplicable, owing to the subsidiary changes induced by bromine. Among other methods, we therefore tried one suggested by the behaviour of benzenediazo-ψ-semicarbazinocamphor towards very dilute alkali, which resolves it into phenylazoimide and camphoryl-ψ-carbamide (Trans., 1906, **89**, 222). After several preliminary failures, however, the method finally adopted was the general one described by Emil Fischer (*Annalen*, 1877, **190**, 96), namely, addition of sodium carbonate to the diazonium salt mixed with hydroxylamine hydrochloride; this action has been studied also by Mai (*Ber.*, 1892, **25**, 372), who, under modified conditions, effected a replacement of the diazo- by the amino-group, and later by Rupe and von Majewski (*Ber.*, 1900, **33**, 3408).

Although we are now able to prepare *p*-hydroxyphenylazoimide in considerable quantity and excellent condition, the early experiments were very discouraging, both as regards quality and yield. We ascribe this to the tendency displayed by the diazotised phenol * to undergo decomposition when the solution of hydroxylamine is added, and find that addition of potassium hydroxide in small proportions at this stage has a marked effect in improving the yield. The exact course of the action is still obscure, but it seems probable that the hydroxylamine forms with the diazo-anhydride a hydroxylamino-derivative which, when treated with potash, undergoes rearrangement, and then loses water.



This appears to us more plausible than the explanation put forward by Mai (*loc. cit.*), according to whom the intermediate stage in the conversion of diazotised toluidine into tolylazoimide is the condensation product, $C_6H_4Me\cdot N\colon N\cdot O\cdot NH_2$, which is represented as then losing water; it is difficult to believe that such a compound would arise from the diazotised aminophenol, which is itself an anhydride.

In its behaviour towards alcoholic potash, *p*-hydroxyphenylazoimide might be expected to behave in a manner recalling either camphorylazoimide or certain aromatic azoimides in which hydrogen has been replaced by a negative group, as, for example, *p*-nitrophenylazoimide, which yields hydrazoic acid and *p*-azoxyphenetole, arising from the corresponding nitrophenol (Noelting, Grandmougin, and Michel, *Ber.*, 1892, **25**, 3328). Neither of these changes has been observed, however, the potassium derivative of *p*-hydroxyphenylazoimide behaving in a distinctive manner which is very interesting. As precipitated by alcoholic potash from a freshly prepared specimen of the phenol in dry ether, the substance is practically colourless, but when a solution in absolute alcohol is warmed, it rapidly becomes intensely blue, and on treatment with ether or chloroform furnishes a dark blue, crystalline potassium derivative which is apparently isomeric with the original substance. During this change there is no liberation of gas, and on acidification, *p*-hydroxyphenylazoimide is recovered, unaccompanied by hydrazoic acid, distinguishing the change from that observed by Curtius, who noticed a blue coloration on dissolving hippurylazoimide in sodium hydroxide (*J. pr. Chem.*, 1895, [ii], **52**, 243).

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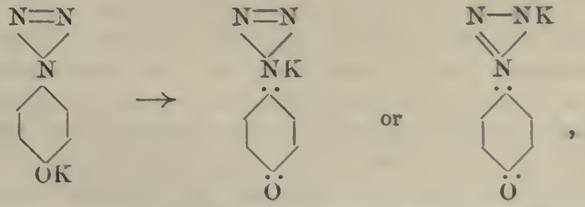
* The present occasion is not suited to a discussion of the constitution of diazotised phenols, and although aware that Wolff (*Annalen*, 1900, **312**, 126) represents them as quinonediazides, and has been supported in this action by Hantzsch (*Ber.*, 1902, **35**, 888), Orton also inclining to this view (Trans., 1903, **83**, 796), we believe that the change under consideration is one of those in which the anhydride formula best meets the facts. It must not be overlooked that other changes also have been found in closer agreement with this representation (Morgan and Micklethwait, Trans., 1905, **87**, 1302, and 1906, **89**, 4).

Before this blue salt was isolated and analysed, we believed the development of colour to be due to indophenol formation, which would indicate the occurrence of the very change we hoped to effect, because an indophenol might be expected to arise from *p*-quinoneimine becoming condensed with unaltered *p*-hydroxyphenylazoimide, to

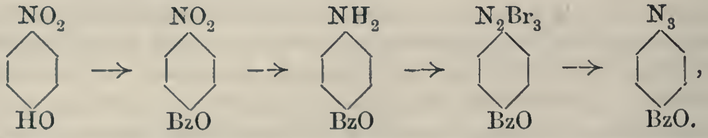
$$O{:}C_6H_4{:}N{\cdot}C_6H_4{\cdot}N_3.$$

Such an action, however, involves loss of nitrogen, and is therefore precluded in the present instance. We are more disposed to think that the case must be parallel with the observation of Loring Jackson and Oenslager (*Ber.*, 1895, **28**, 1614), who found that when *p*-quinone and sodium phenoxide are mixed in ether, a deep blue precipitate is formed having the composition $C_6H_4O_2,2C_6H_5{\cdot}ONa$. In other words, it appears to us quite likely that the colourless potassium derivative is capable of undergoing transformation into a quinonoid modification,

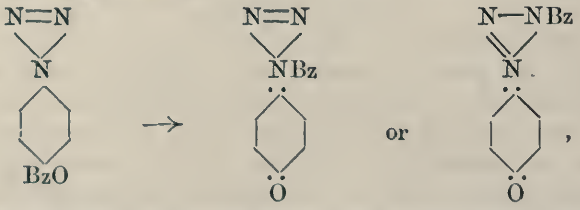


which immediately combines with unaltered isomeride to produce a deep blue substance. We have made many attempts to isolate the benzoyl and *m*-nitrobenzoyl derivatives in quinonoid modifications, hitherto unsuccessfully, but it is significant that specimens of these compounds prepared from the blue derivative, although melting at the same temperature as those from the colourless variety, are uniformly much darker coloured, whilst in the case of the *m*-nitro-compound the crystalline habit appears to be different.

Even when the colourless potassium derivative is employed as the starting material for the benzoic ether, there is considerable difficulty in obtaining the product free from colour, and at first it appeared uncertain whether this compound might not be the quinonoid variety; accordingly we prepared it by a method which renders that possibility remote, from *p*-nitrophenol, as follows,



obtaining a benzoyl derivative identical with the one furnished by the colourless potassium derivative of *p*-hydroxyphenylazoimide. Hence we are led to the conclusion that the benzoyl derivative when freshly prepared from a good specimen of the colourless alkali compound contains at most a trace of the quinonoid variety, which is perceptibly augmented, however, in the product from the blue modification. Although it may appear somewhat bold to suggest the change in question, namely,

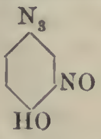


external justification may be found in some recent experiments by Auwers (*Annalen*, 1904, **332**, 159), who gives evidence of the change

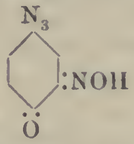
$$BzO{\cdot}C_6H_2Br_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_5 \longrightarrow HO{\cdot}C_6H_2Br_2{\cdot}CH_2{\cdot}NBz{\cdot}C_6H_5.$$

It is true that this is confined to ortho-derivatives, and does not take place with meta- and para-compounds, but on the other hand the recognition by Hantzsch and Gorke of *aci*-nitrophenol esters among the products of the action between anhydrous alkyl halides and the carefully dried silver salts of nitrophenols (*Ber.*, 1906, **39**, 1073) places the change in question within the bounds of probability. Moreover, just as the nitrophenols yield a solution in alkali which must be regarded as containing the *aci*-nitrophenol salt, $O{:}C_6H_4{:}NO{\cdot}OR$, in preponderating amount, so the colourless potassium derivative of *p*-hydroxyphenylazoimide, when dissolved in water, changes spontaneously into the coloured variety, and very rapidly when warmed. We hope, however, to gain more information on this point by studying the meta- and ortho-compounds, which are now in hand.

One point remains to be noticed before describing the experiments. In the hope of obtaining the nitrosophenol,



or



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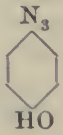
we treated *p*-hydroxyphenylazoimide with nitrous acid, which converts it, however, into the azoimide derivative of *o*-nitrophenol; previous cases of this action have been recorded, salicylic acid, for example, undergoing nitration in the same circumstances, whilst pyrene is converted into the nitro-derivative when an ethereal solution, floating on concentrated aqueous potassium nitrite, is slowly treated with very dilute sulphuric acid. It is noteworthy that whilst *p*-hydroxyphenylazoimide, although volatile in steam, rapidly undergoes deterioration with boiling water, the *nitro*-derivative is quite stable, and may be purified by steam distillation; moreover, the potassium derivative of the latter substance is distinguished, by its stability, from the colourless *p*-hydroxyphenylazoimide compound, which suggests that the formation of a blue derivative is suspended by the stronger demand of the nitro-group for metal.

EXPERIMENTAL.

p-*Hydroxyphenylazoimide*,



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An ice-cold solution of *p*-aminophenol hydrochloride, prepared from 30 grams, and 200 c.c. of hot water, was treated with 50 c.c. of concentrated hydrochloric acid, and slowly diazotised with 15 grams of sodium nitrite in 50 c.c. of ice-water; 20 grams of hydroxylamine hydrochloride dissolved in 50 c.c. of water were then added, the mixture being promptly poured into 1200 c.c. of ice-cold water in which 150 grams of anhydrous sodium carbonate had been dissolved. The liquid became intensely yellow, but after a brief interval some tarry material floated to the surface of the solution, which was now turbid and brown, whilst an intensely sweet taste, characteristic of *p*-hydroxyphenylazoimide, became perceptible. About this time a moderate effervescence began, and, becoming quite brisk after fifteen minutes, 50 c.c. of a 25 per cent. solution of potassium hydroxide were added, thus checking the gas evolution, and the liquid, now amounting to 1750 c.c., was freed from tar by passage through a large fluted filter. The alkaline filtrate was next treated with 20 per cent. acetic acid until brisk effervescence occurred, but excess of the acid need not be used, as the hydroxyphenylazoimide is quite easily extracted by ether from its solutions in sodium carbonate and bicarbonate; moreover, it is sparingly soluble in water which is saturated with ether, and consequently three separate extractions with 300 c.c. of the solvent were sufficient to remove it from the salt solution.

The combined ethereal solutions were very dark brown, and if dried without further treatment yielded a most unsatisfactory specimen of the azoimide, which is most conveniently isolated in the form of its potassium derivative; dilute potash followed by a 50 per cent. solution precipitated the potassium derivative in lustrous plates, but these crystals were almost invariably dark brown or greenish-brown, and could not be decolorised by recrystallisation. A white, or at most slightly yellow, specimen of the potassium derivative can be obtained, however, by shaking the ethereal solution several times with aqueous sodium carbonate until the colour is reduced from dark brown to pale pink; the first extracts are almost black, and the final ones bluish, twenty or twenty-five extractions being necessary. The ethereal solution may be dried with calcium chloride, but anhydrous sodium sulphate is to be preferred, because the dissolved material undergoes resinification more quickly when in contact with the former material. From the dried solution the potassium derivative was prepared by adding 8 grams of potassium hydroxide dissolved in 40 c.c. of absolute alcohol, which precipitated 18·5 grams of a colourless material quickly assuming a faint greenish-yellow tinge; this derivative was filtered with the aid of a pump, washed with absolute ether, and dried in a desiccator protected from light. The mother liquor unavoidably contained some of the azoimide derivative, because if potash is in excess, the precipitate is contaminated with free alkali.

The *p*-hydroxyazoimide, in the form of a colourless oil, has been obtained by adding acetic acid to an aqueous solution of the white potassium derivative, and on evaporating an ethereal solution at the ordinary temperature in absence of water, there was deposited a viscous oil which quickly solidified in a freezing mixture and melted again at about 20°; but this product soon became almost black in the desiccator, and an attempt to purify it by steam distillation was unsuccessful, as it decomposes profoundly when heated with water. Distillation under reduced pressure was equally disappointing. Under 0·5—1 mm., ebullition appeared to begin at about 150°, but suddenly gas was evolved in torrents, and an alarming explosion took place, pulverising the porcelain dish which served as an oil-bath; attempts to obtain the substance in a form suitable for analysis have been abandoned in consequence. The azoimide is a definite substance, however, giving rise to certain derivatives described below; it has a strongly sweet taste, and the odour suggests phenol and hydrazoic acid, producing in a modified degree the characteristic throbbing at the base of the forehead when the vapour is inhaled. Ferric chloride develops a pink coloration; reduction with stannous chloride resolves it into *p*-aminophenol and ammonia.

The Benzoyl Derivative.—This compound is readily obtained by shaking benzoyl chloride with an alkaline solution of the colourless or blue potassium derivatives described below. It is readily soluble in ethyl acetate, acetone, benzene, pyridine, methyl alcohol, or ethyl alcohol, but only moderately in light petroleum boiling at 50—60°, and is most conveniently crystallised from the last-named, which deposits it on cooling in lustrous needles, melting at 80—81°. Although stable when protected from light, it becomes opaque and dull on exposure, this change in appearance being accompanied by a fall in the melting point, which becomes indefinite at 70—75°. On one occasion we obtained colourless crystals of the benzoyl derivative, but usually the substance is pale brown, and there appears to be no difference in the melting point of various specimens.

Considerable difficulty has been experienced in the estimation of carbon, the percentage of which frequently appeared to be 0·8—1·2 per cent. in excess of that required by the formula; this was observed also in connexion with the *m*-nitrobenzoyl derivative described below, and it has been recorded that formazyl compounds present great difficulty (Bamberger, *Ber.*, 1894, **27**, 157), whilst azines gave results approximating to 8 per cent. surplus of nitrogen (Klingemann, *Ber.*, 1889, **22**, 3064). Satisfactory results were obtained ultimately by using both silver and copper reducing spirals amounting to 25 cm. in length.

0·1986 gave 0·4757 CO_2 and 0·0723 H_2O. C = 65·33; H = 4·04.
0·1294 ,, 19·2 c.c. of nitrogen at 19° and 773 mm.; N = 17·64.
$C_{13}H_9O_2N_3$ requires C = 65·27; H = 3·77; N = 17·57 per cent.

A determination of molecular weight gave the average value 203 in benzene, that calculated for $C_{13}H_9O_2N_3$ being 239. The behaviour of the substance towards 80 per cent. sulphuric acid recalls that of other azoimides, nitrogen being set free suddenly in quantity representing two-thirds of the total content.

0·2272 gave 22·4 c.c. of nitrogen at 20° and 751 mm. N = 11·35.
$C_{13}H_9O_2N_3$ requires 2/3 N = 11·71 per cent.

The benzoyl derivative is readily hydrolysed by alcoholic potash and hydrochloric acid, the same effect being produced by heating with hydroxylamine acetate in absolute alcohol. It is indifferent towards aqueous stannous chloride, but an alcoholic solution reduces the substance very readily, forming benzoyl-*p*-aminophenol and ammonia, unaccompanied by nitrogen; this behaviour is distinctive from that of camphorylazoimide, which changes quantitatively into aminocamphor and nitrogen.

The m-*Nitrobenzoyl Derivative.*—The substance is prepared by shaking an alkaline solution of the potassium derivative with finely divided *m*-nitrobenzoyl chloride, and recrystallising the product from boiling absolute alcohol, which deposits long, lustrous, faintly yellow needles melting at 118°.

0·1700 gave 0·3442 CO_2 and 0·0537 H_2O. C = 55·21; H = 3·51.
0·1790 ,, 30·6 c.c. of nitrogen at 20° and 756 mm. N = 19·81.
$C_{13}H_8O_4N_4$ requires C = 54·93; H = 2·82; N = 19·71 per cent.

The *m*-nitrobenzoyl derivative is very sensitive to light, which causes the crystals to become deep yellow and depresses the melting point. It is sparingly soluble in cold alcohol, and almost insoluble in petroleum, which dissolves it sparingly when boiled; in benzene chloroform or hot alcohol it is readily soluble.

The Methyl Ether.—This compound was first obtained by Rupe and von Majewski (*Ber.*, *loc. cit.*) from diazotised *p*-anisidine, and later by one of us from *p*-methoxybenzenediazo-ψ-semicarbazinocamphor and aqueous alkali (Trans., 1906, **89**, 238). We have prepared it again from the former source, and confirm the observations of the authors mentioned, obtaining the substance from a petroleum solution in lustrous, yellowish plates melting at 35°; an attempt to distil it under 29 mm. pressure was unsuccessful, decomposition occurring at 150°.

The Colourless Potassium Derivative.—When freshly prepared from a carefully purified ethereal solution of the azoimide, the potassium derivative is colourless, and forms colourless solutions in water and cold alcohol; on adding ether or chloroform to the latter, it is precipitated in lustrous plates which usually have a brownish tinge, and these crystals appear to contain alcohol of crystallisation, although our analytical results agree only approximately with those required by calculation.

0·2538 gave 40·7 c.c. of nitrogen at 19° and 750 mm. N = 18·64.
0·2451 ,, 0·1011 K_2SO_4. K = 18·48.
$C_6H_4ON_3K$ requires N = 24·28; K = 22·54 per cent.
$C_6H_4ON_3K,C_2H_6O$,, N = 19·18; K = 17·81 ,,

These figures might be expected from a specimen containing a small proportion of alkali carbonate, and are confirmed by the decomposition with 80 per cent. sulphuric acid:

0·2488 gave 25·6 c.c. of nitrogen at 20° and 750 mm. N = 11·82.
$C_6H_4ON_3K,C_2H_6O$ requires 2/3 N = 12·79 per cent.

When the colourless potassium derivative is covered with a mixture of concentrated hydrochloric and nitric acids (1 : 1), a very vigorous action ensues, and a quantitative yield of tetrachloroquinone is produced.

The Blue Potassium Derivative.—Although when freshly prepared the potassium derivative is practically colourless and forms a colourless solution in water, the dry substance becomes green during a few hours even when protected from light, and then dissolves in water with a bluish-green shade. If such a solution is gently heated, the colour rapidly intensifies to the magnificent "King's blue" associated with a successful application of the Liebermann test for nitroso-compounds, and evolution of gas occurs simultaneously. The latter change appears to follow the development of colour, because we have isolated a definite blue derivative by warming the colourless compound with absolute alcohol during one hour at 50—60° and adding dry ether to the deep blue liquid, when a lustrous, blue, crystalline precipitate is formed; during this process, moreover, there is no evolution of gas, provided water is excluded from the system.

The product dissolves freely in water, developing the rich colour mentioned above, and as the aqueous solution evolves gas when heated, it appears that the change undergone by the colourless derivative when the solution in water is heated consists of transformation into the coloured variety followed by decomposition involving liberation of gas; if this more profound alteration is allowed to proceed, the pure blue colour changes to dirty greenish-blue, and acidification yields a reddish-brown precipitate which is soluble in alkali, but has not yet furnished a homogeneous, crystalline material. Benzoquinone, although carefully sought, has not been recognised in the product.

Analysis gave results indicating isomerism between this compound and the colourless variety:

0·2290 gave 35·0 c.c. of nitrogen at 20° and 751 mm. N = 18·40.

0·1567 „ 0·0728 Pt. K = 18·58.

$C_6H_4ON_3K,C_2H_6O$ requires N = 19·18; K = 17·81 per cent.

Two-thirds of the nitrogen was liberated by cold 80 per cent. sulphuric acid:

0·2234 gave 22·6 c.c. of nitrogen at 20° and 750 mm. N = 11·63.

The same proportion was gradually evolved on boiling the aqueous solution continuously:

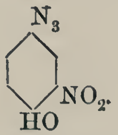
0·2524 gave 28·2 c.c. of nitrogen at 20° and 760 mm. N = 13·21.

$C_6H_4ON_3K,C_2H_6O$ requires 2/3 N = 12·79 per cent.

During the latter decomposition a very small proportion of ammonia was produced, and identified in the form of platinichloride.

The blue derivative readily undergoes hydrolytic dissociation when the aqueous solution is diluted, the intense blue colour being quickly destroyed, and changing to delicate pink; in this solution the blue colour is immediately restored by alkali. If a concentrated solution is acidified with an organic or mineral acid, the liquid becomes red, and the blue colour is restored on adding alkali; the hydroxyphenylazoimide liberated by acids appears to have the properties of the original material, but the solid potassium derivative obtained from it is bluish-green. Moreover, although the benzoyl and *m*-nitrobenzoyl derivatives obtained by agitating the blue derivative in water with the respective chlorides melted at the temperatures just recorded, in each case the specimens were deep red, and the nitro-compound crystallised in hard, lustrous prisms instead of silky needles. The methoxy-compound obtained by heating the blue derivative in absolute alcohol with methyl iodide was identical with that prepared from *p*-anisidine, however, although the yield was very bad, more than half the material remaining in the distillation flask in the form of a red, amorphous solid.

3-*Nitro*-4-*hydroxyphenylazoimide*,



Five grams of the colourless potassium derivative of *p*-hydroxyphenylazoimide dissolved in 200 c.c. of water were treated with 15 c.c. of hydrochloric acid and cooled with ice; to the well-stirred liquid a solution containing 4 grams of sodium nitrite was added slowly, the first drop producing turbidity soon followed by yellow crystals, unaccompanied by gas evolution. After one hour the product was extracted with ether, the ether evaporated, and the residue distilled in a current of steam, which carried over bright yellow needles weighing 2·5 grams; recrystallisation from petroleum followed by alcohol raised the melting point to 91°.

0·1148 gave 31·3 c.c. of nitrogen at 21° and 752 mm. N = 31·32.

$C_6H_4O_3N_4$ requires N = 31·11 per cent.

The nitro-compound, which has a pungent, quinone-like odour in steam, is obtained also when an ethereal solution of *p*-hydroxyphenylazoimide is treated with nitrosyl chloride in glacial acetic acid. It is slightly soluble in water, and crystallises in beautiful reddish-orange prisms from both alcohol and petroleum; the crystals become dark brown when exposed to light, and owing to the volatility of the substance the specimen bottle is quickly covered with a deep red film.

The *potassium* derivative forms dark red needles, and the aqueous solution, which resembles that of *o*-nitrophenol in alkali, becomes first yellow, then colourless when treated with acid, the neutral stage being well defined.

The *benzoyl* derivative, prepared by the pyridine method, crystallises from alcohol in long, lustrous, colourless needles melting at 103° after sintering a few degrees lower.

0·1454 gave 24·6 c.c. of nitrogen at 20° and 758 mm. N = 19·67.

$C_{13}H_8O_4N_4$ requires N = 19·72 per cent.

The substance is readily soluble in hot petroleum, from which it crystallises in lustrous plates; it dissolves freely in chloroform, separating in needles on adding petroleum. The crystals become pink when exposed to light.

Having noticed that *m*-nitrophenylazoimide is quickly reduced to *m*-nitraniline by alcoholic ammonium sulphide, we applied this process to the identification of the nitrohydroxyphenylazoimide, because the product which should arise by reduction, namely, *o*-nitro-*p*-aminophenol, has been characterised by Friedländer and Zeitlin (*Ber.*, 1894, **27**, 196), who obtained it by the action of 66 per cent. sulphuric acid on *m*-nitrophenylazoimide:

$$NO_2\cdot C_6H_4\cdot N_3 + H_2O = NO_2\cdot C_6H_3(OH)\cdot NH_2 + N_2.$$

Hydrogen sulphide was passed into a solution containing 1 gram of nitrohydroxyphenylazoimide in alcoholic ammonia, when the dark colour became intensified, and brisk effervescence occurred; the solution was filtered from sulphur and evaporated, the residue being recrystallised from boiling petroleum, which deposited long, silky, dark red needles having a brown lustre, and melting at 131°. Friedländer and Zeitlin having given 126—128° as the melting point, a specimen was prepared by their method, and found to be identical with our own.

3-*Nitro*-4-*hydroxyphenylazoimide from* p-*Hydroxyphenylhydrazine.*

The foregoing method for preparing the nitro-compound being one which might have been expected to yield the corresponding nitroso-derivative, it appeared desirable to study the action of nitrous acid upon *p*-hydroxyphenylhydrazine (Altschul, *J. pr. Chem.*, 1898, [ii], **57**, 203). Five grams of the hydrochloride were dissolved in 100 c.c. of 5 per cent. hydrochloric acid, cooled with ice, and treated with 8 grams of sodium nitrite; yellow crystals quickly separated, and by the treatment previously applied, 3-nitro-4-hydroxyphenylazoimide was obtained in yellow crystals melting at 91°, which do not depress the melting point of the former specimen when mixed with it.

In the paper quoted, Altschul described the nitrosamine of *p*-hydroxyphenylhydrazine as consisting of brownish crystals characterised by the stupefying odour of nitrosophenylhydrazine; the melting point was not recorded, however, and we believe this specimen to have been very impure, because repetition of the experiment under the conditions prescribed by Altschul gave snow-white, lustrous needles. This product was odourless, and could be recrystallised from warm methyl alcohol, when it melted at 123—124°; it has been preserved during two months without undergoing decomposition, and gives the Liebermann reaction very well defined in all stages. The substance is very sensitive to alkalis, and is decomposed by warm mineral acids, producing a quinone-like odour, which probably accounts for the observation of Altschul.

Preparation of 4-*Benzoxyphenylazoimide from* p-*Nitrophenol.*

The difficulty experienced in obtaining a colourless specimen of the benzoyl derivative of *p*-hydroxyphenylazoimide, coupled with the uncertainty of the earlier analytical results, rendered it important to prepare the substance by an independent method, if possible one excluding the probability of the substance having a quinonoid structure. This has been carried out by converting *p*-nitrophenol into the benzoyl derivative, reducing this to *p*-benzoxyaniline, and transforming the diazonium salt of this base into the perbromide, which, on treatment with ammonia, yielded *p*-benzoxyphenylazoimide.

The benzoyl derivative of *p*-nitrophenol was obtained quantitatively by heating 70 grams with 62 grams of benzoyl chloride until hydrogen chloride was no longer evolved, dissolving the hard cake in boiling glacial acetic acid and pouring the solution into water. The readiness with which the ester is hydrolysed not only precludes its preparation by the Schotten-Baumann method; it also renders the reduction a matter of considerable difficulty. Hübner (*Annalen*, 1881, **210**, 379) effected this by using alcoholic hydrochloric acid and tin, but on repeating his experiment we obtained less than 5 per cent. of the base, the remaining ester becoming hydrolysed. Equally unsuccessful were attempts to reduce with zinc dust and water, alcoholic ammonium sulphide, iron with acetic acid, and aluminium amalgam in moist ether, but a good yield of *p*-benzoxyaniline was ultimately obtained by reducing the nitro-compound with alcoholic acetic acid and zinc. Fifty grams of benzoylated *p*-nitrophenol were suspended in 500 c.c. of alcohol mixed with 200 c.c. of 50 per cent. acetic acid; to the well-stirred liquid 100 grams of zinc dust made pasty with alcohol were added at such a rate as to keep the temperature below 40°, and when this amount of metal had been used, 50 c.c. of glacial acetic acid were added, and the liquid stirred until potash no longer developed a yellow coloration when heated with the alcoholic liquid. On filtering from zinc it was necessary to wash the latter with boiling water as well as alcohol, because a portion of the base remains in the form of a double salt which is insoluble in alcohol, but is decomposed by hot water; the filtrate deposited 40 grams of pure, crystalline, *p*-benzoxyaniline. The conversion of this compound into the azoimide was attempted first by Fischer's method, but a more satisfactory yield was obtained by converting the diazonium salt into the perbromide, and treating this with ammonia.

p-*Benzoxydiazobenzene Perbromide*, $C_6H_5 \cdot CO \cdot O \cdot C_6H_4 \cdot N_2Br_3$, was prepared by diazotising with 10 grams of sodium nitrite in 20 c.c. of water an ice-cold paste containing 30 grams of *p*-benzoxyaniline, 150 c.c. of glacial acetic acid, and 30 c.c. of hydrobromic acid (sp. gr. 1·42), afterwards adding to the filtered solution 33 grams of bromine dissolved in 30 c.c. of hydrobromic acid; the liquid was diluted with its own volume of water, and the filtered perbromide, of which the yield was quantitative, recrystallised from hot, absolute alcohol, forming beautiful, lustrous, orange needles, decomposing at 106—108°.

0·1417 gave 0·1700 AgBr. Br = 51·06.

$C_{13}H_9O_2N_2Br_3$ requires Br = 51·61 per cent.

It was necessary to heat the Carius tube at 400—420° during eight hours; estimations at 260—300° and 320—360° gave 42 per cent. and 50 per cent. of bromine respectively.

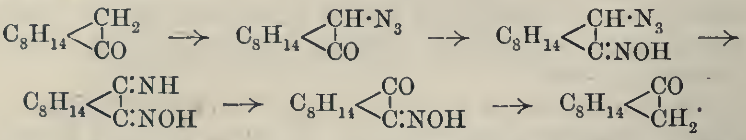
The conversion of the perbromide into the azoimide took place in the ordinary fashion, and the resulting material was identical with the substance obtained on benzoylating *p*-hydroxyphenylazoimide, thus establishing the constitution of this compound. Nevertheless, it is not a convenient source of the azoimide itself, because although very readily hydrolysed, separation of the latter from the product is a troublesome process.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

LXXX.—*Studies in the Camphane Series. Part XXIII. Oximes of Camphorylsemicarbazide and Camphorylazoimide.*

By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

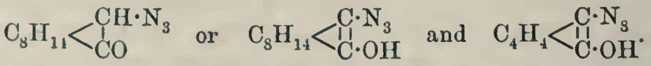
DURING the past four years various unsuccessful attempts have been made by one of us to obtain a structural isomeride of camphor through the missing monoxime of camphorquinone isomeric with *iso*nitrosocamphor, and a favourable opportunity to produce the monoxime appearing to follow from the observation that a trace of alcoholic potash eliminates two-thirds of the nitrogen from camphorylazoimide, leaving iminocamphor (Trans., 1905, 87, 826), we hoped to complete the following series:



$$C_8H_{14}<\begin{array}{l}CH_2\\|\\CO\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CH{\cdot}N_3\\|\\CO\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CH{\cdot}N_3\\|\\C{:}NOH\end{array} \rightarrow$$

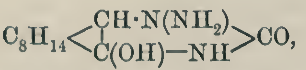
$$C_8H_{14}<\begin{array}{l}C{:}NH\\|\\C{:}NOH\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CO\\|\\C{:}NOH\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CO\\|\\CH_2\end{array}.$$

On preparing the oxime of camphorylazoimide, however, we were disappointed to find it quite indifferent towards cold alcoholic potash, so that the next step in the series could not be taken. Another distinctive feature of the substance is its resistance to light, which quickly renders the colourless, transparent crystals of the azoimide opaque and pink, whereas the oxime has now been exposed during twelve months without undergoing apparent change. In seeking the explanation of these differences, it seemed possible that the activity of the azoimide was due to enolisation, a process which would not be possible in the oxime, and we are therefore studying the hydroxyphenylazoimides with a view to making comparison between camphorylazoimide and *o*-hydroxyphenylazoimide (compare Trans., this vol., p. 855):



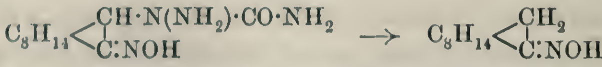
$$C_8H_{14}<\begin{array}{l}CH{\cdot}N_3\\|\\CO\end{array} \text{ or } C_8H_{14}<\begin{array}{l}C{\cdot}N_3\\||\\C{\cdot}OH\end{array} \text{ and } C_4H_4<\begin{array}{l}C{\cdot}N_3\\||\\C{\cdot}OH\end{array}.$$

In conjunction with these experiments we have investigated the behaviour of camphoryl-ψ-semicarbazide towards hydroxylamine, and have incidentally observed a case of isomerism which appears to merit description. For reasons given in previous papers (Trans., 1905, 87, 110 and 722), camphoryl-ψ-semicarbazide is represented by the formula



$$C_8H_{14}<\begin{array}{l}CH{\cdot}N(NH_2)\\|\\C(OH){-}NH\end{array}>CO,$$

and on heating the acetate in alcohol with the acetate of hydroxylamine, there is produced an oxime which has $[\alpha]_D$ 105·4° in glacial acetic acid, and melts at 242°; we represent this compound as derived from normal camphorylsemicarbazide, principally because hot Fehling's solution, which oxidises camphoryl-ψ-semicarbazide itself to camphor, converts the oxime into camphoroxime:

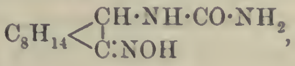


$$C_8H_{14}<\begin{array}{l}CH{\cdot}N(NH_2){\cdot}CO{\cdot}NH_2\\|\\C{:}NOH\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CH_2\\|\\C{:}NOH\end{array}.$$

It has been shown already that camphoryl-ψ-semicarbazide is characterised by the readiness with which it undergoes condensation with aldehydes, and as the oxime would appear to contain a primary semicarbazide nucleus, we expected to find that this compound also would combine freely with aldehydes. That, however, is not the case. Condensation products have been obtained, it is true, from benzaldehyde, *m*-nitrobenzaldehyde, and furfuraldehyde, but only with great difficulty, and experiments with other aldehydes failed to yield derivatives. Moreover, the compounds obtained from the aldehydes mentioned are resolved by dilute acids into their components so easily as to distinguish them sharply from camphoryl-ψ-semicarbazones. The unusually high specific rotatory power which characterised the latter group is not observed among the members of the oxime series.

By the action of acids on the oxime of camphorylsemicarbazide (m. p. 242°), there is produced an isomeric substance melting at 222°, the converse change being effected by warm, dilute potassium hydroxide. This oxime is lævorotatory, and is further distinguished from the original modification by the readiness with which hydroxylamine is eliminated under the influence of acids, regenerating camphoryl-ψ-semicarbazide. This behaviour on the part of a substituted camphoroxime is quite unusual, and as far as we know, unique, because one of the most conspicuous features of camphoroxime, distinguishing it from the majority of ketoximes, is the tenacity with which the oximino-group resists the action of hydrolytic agents.

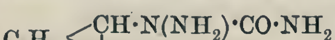
Moreover, the occurrence of isomerism among the substitution products of camphoroxime has not been observed hitherto, and in this connexion the properties of a substance first described by Lapworth and Harvey (Trans., 1902, **81**, 553) appear highly interesting. These authors warmed the hydrochloride of aminocamphoroxime with potassium cyanate, obtaining the oxime of camphorylcarbamide,



$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CO\cdot NH_2\\ |\\ C:NOH\end{matrix},$$

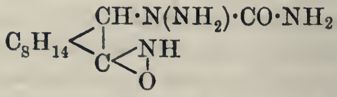
which we prepared subsequently by the action of hydroxylamine on camphorylcarbamide and its *pseudo*-modification (Trans., 1905, **87**, 114). They noted two crystalline forms, needles and plates, both of which appeared to melt at 203—204°; on one occasion, however, they found the plates melted at 158—159°, immediately solidified, and melted again at 203—204°. In the light of our own experiments, it appears to us probable that a specimen of the oxime which melts at 203—204° contains two modifications, because we have raised the melting point to 212° by repeated crystallisation, and then, by the action of cold hydrochloric acid, converted it into a modification which, when crystallised from methyl alcohol, partly fuses at about 180°, immediately resolidifies, and finally melts at 202°.

Much remains to be accomplished before the exact relation between the two oximes of camphorylsemicarbazide can be established, but the existence of camphoroxime and its derivatives in one form only has long been a puzzling circumstance to workers on the subject, and makes it worth while to record the existence of these two compounds. The most significant point as regards this relationship, however, is the facility with which hydroxylamine is eliminated from the modification which melts at 222°. The behaviour of the benzylidene derivative towards acids indicates that the less fusible modification does not thus lose the oximino-group, and the natural conclusion is that the two compounds are oxime and *iso*-oxime,



$$C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\cdot CO\cdot NH_2\\ C{:}NOH\end{matrix}$$

and

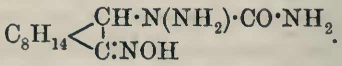


$$C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\cdot CO\cdot NH_2\\ |\\ C<\begin{matrix}NH\\ |\\ O\end{matrix}\end{matrix}$$

because the only camphor derivative in which the *iso*-oxime structure has been conclusively recognised, namely, the *N*-methyl ether of *iso*nitrosocamphor, is hydrolysed immediately by warm, dilute, mineral acids, yielding camphorquinone and β-methylhydroxylamine (Trans., 1904, 85, 896).

EXPERIMENTAL.

Oxime of Camphorylsemicarbazide,



$$C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\cdot CO\cdot NH_2\\ C{:}NOH\end{matrix}.$$

One hundred grams of camphoryl-ψ-semicarbazide nitrate were converted into the acetate, and heated in 700 c.c. of absolute alcohol with 50 grams of hydroxylamine hydrochloride and 50 grams of crystallised sodium acetate dissolved in water; after four hours the liquid was diluted, and evaporated until crystals began to separate, 70 grams being thus obtained. It was found that the yield is greatly diminished if the alcohol is removed before adding water, owing to the hydrolytic action of the free acetic acid; moreover, much time is saved by using the acetone compound of the ψ-semicarbazide instead of the acetate, the yield of oxime being the same.

The substance was recrystallised from boiling absolute alcohol, separating in lustrous, transparent, six-sided plates; it melts at 242°, with violent intumescence:

0·1757 gave 0·3520 CO_2 and 0·1304 H_2O. C = 54·64; H = 8·25.

0·2436 ,, 49·8 c.c. of nitrogen at 19° and 766 mm. N = 23·64.

$C_{11}H_{20}O_2N_4$ requires C = 55·00; H = 8·33; N = 23·33 per cent.

A solution containing 0·1025 gram in 25 c.c. of pyridine gave α_D 0°40′ in a 2-dcm. tube, whence $[\alpha]_D$ 81·3°, and 0·2114 gram dissolved in 25 c.c. of glacial acetic acid gave α_D 1°47′, corresponding to $[\alpha]_D$ 105·4°. The oxime is insoluble in petroleum, and dissolves very sparingly in boiling acetone, chloroform, or ethyl acetate; it is moderately soluble in hot alcohol, cold pyridine, or hot nitrobenzene;

dissolving readily in cold glacial acetic acid, from which it separates on considerable dilution with water. The substance dissolves in dilute aqueous alkalis, being reprecipitated by acids, but is insoluble in sodium carbonate. The alcoholic solution gives a mirror when warmed with ammoniacal silver oxide, but it is indifferent to ferric chloride, even on boiling.

The action of Fehling's solution on the oxime indicates very clearly the position of the oximino-group. This agent has been shown to oxidise camphoryl-ψ-semicarbazide to camphor, with simultaneous elimination of cyanic acid; the oxime also reduces Fehling's solution on warming, the product consisting of camphoroxime, which can be extracted by ether in the form of a soluble copper derivative.

The Isomeric Oxime.—When dry hydrogen chloride is passed into a suspension of the finely powdered oxime in benzene no change occurs, but if solid sodium carbonate is added to a solution of the oxime in 20 per cent. sulphuric acid or concentrated hydrochloric acid, the colourless, crystalline precipitate is found to be distinct from the original oxime, although isomeric with it, whilst the filtrate reduces cold Fehling's solution. The elimination of hydroxylamine to which this reduction is due makes it impossible to convert the oxime into the isomeride quantitatively, because the dissolution in acid proceeds very slowly, and before it is complete the product has begun to lose hydroxylamine. The isomeride dissolves sparingly in boiling alcohol, from which it crystallises in flat, lustrous needles, melting with decomposition at 222°.

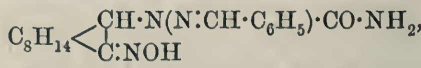
0·1811 gave 0·3634 CO_2 and 0·1393 H_2O. C = 54·73; H = 8·54.
0·1356 „ 27·9 c.c. of nitrogen at 24° and 766 mm. N = 23·26.
$C_{11}H_{20}O_2N_4$ requires C = 55·00; H = 8·33; N = 23·33 per cent.

A solution containing 0·1015 gram in 25 c.c. of pyridine gave α_D $-0°23'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-37·7°$. The substance is insoluble in petroleum, and dissolves very sparingly in boiling chloroform, being slightly more soluble in boiling ethyl acetate; cold pyridine dissolves it less readily than the original oxime.

Before this compound was analysed, it was believed to be the anhydride of the dextrorotatory oxime, because the latter is regenerated when the solution is heated with aqueous potash; the cold agent has no effect upon it, but warming the liquid effects dissolution, and on neutralising the diluted solution with hydrochloric acid, the crystalline precipitate consists of the dextrorotatory oxime. The isomerides are distinguished by their behaviour towards alcoholic ferric chloride, which develops with the lævorotatory oxime a grass-green coloration, doubtless due to the hydroxylamine eliminated by acids, because the colour of the liquid resembles exactly that produced by ferric chloride and hydroxylamine hydrochloride. The readiness with which hydroxylamine is eliminated is further shown by the behaviour of Fehling's solution, which has no action on a cold alkaline suspension of the lævorotatory oxime; if, however, the latter is dissolved in dilute hydrochloric acid, and promptly rendered alkaline, Fehling's solution is reduced without warming.

Action of Nitrous Acid.—Five grams of the dextrorotatory oxime were dissolved in 50 c.c. of 20 per cent. sulphuric acid and cooled with ice during the gradual addition of 16 c.c. of a 20 per cent. solution of sodium nitrite; no marked change occurred until 13 c.c. had been added, when suddenly a flocculent precipitate appeared in the somewhat turbid liquid. On spreading the filtered material over porous earthenware, it was found to be yellow and slimy, but when exposed to air it gradually became pale and friable, liberating cyanic acid; when quite hard and odourless the product was crystallised from absolute alcohol, and found to consist of camphorylazoimide, melting at 67°. The filtrate from the slimy precipitate was warmed to about 80°, when brisk evolution of cyanic acid took place, and camphorylazoimide separated.

Condensation of the Camphorylsemicarbazide Oxime with Aldehydes.



The *benzylidene* compound, $C_8H_{14}<\begin{matrix}CH\cdot N(N{:}CH\cdot C_6H_5)\cdot CO\cdot NH_2\\ |\\ C{:}NOH\end{matrix}$, was obtained by heating 5 grams of the oxime in alcohol with 3 grams of benzaldehyde and a few drops of ammonia during four hours, a preliminary experiment having shown that condensation does not occur unless the liquid is faintly ammoniacal; the product was crystallised from acetone and then twice from hot alcohol, which yielded lustrous, transparent prisms, melting with decomposition at 205°:

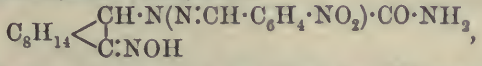
0·1919 gave 0·6077 CO_2 and 0·2591 H_2O. C = 63·96; H = 8·23.
0·2936 „ 38·8 c.c. of nitrogen at 17° and 742 mm. N = 15·30.
$C_{18}H_{24}O_2N_4$ requires C = 65·85; H = 7·31; N = 17·07.
$C_{18}H_{24}O_2N_4 + C_2H_6O$ „ C = 64·17; H = 8·02; N = 14·97 per cent.

A solution containing 0·2612 gram in 25 c.c. of chloroform gave α_D 2°18′ in a 2-dcm. tube, whence $[\alpha]_D$ 110·1°. The substance is insoluble in petroleum, and is only moderately soluble in hot benzene, but it dissolves readily in ethyl acetate, and freely in chloroform and pyridine; when covered with methyl alcohol, ethyl alcohol, or acetone, the compound absorbs the solvent, and dissolves only on heating with a further quantity. Cold Fehling's solution has no action, but is reduced on boiling, and ammoniacal silver oxide also undergoes slight reduction when warmed with the alcoholic solution.

An attempt to prepare the benzylidene compound by heating benzaldehyde camphoryl-ψ-semicarbazone in absolute alcohol with hydroxylamine acetate was unsuccessful, the oxime of camphorylsemicarbazide being produced instead.

When the finely-powdered benzylidene compound was covered with cold 20 per cent. sulphuric acid, the odour of benzaldehyde slowly became perceptible, but the solid did not disappear; after four weeks the filtrate, when rendered alkaline, reduced cold Fehling's solution immediately, whilst the solid contained the lævorotatory oxime and benzaldehyde camphoryl-ψ-semicarbazone. Thus, the action of acid first eliminates benzaldehyde and converts a portion of the regenerated oxime into its isomeride; this loses hydroxylamine, forming camphoryl-ψ-semicarbazide, which at once combines with the liberated benzaldehyde.

The m-*nitrobenzylidene* compound,



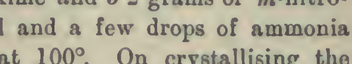
$$C_8H_{14}<\begin{matrix}CH\cdot N(N{:}CH\cdot C_6H_4\cdot NO_2)\cdot CO\cdot NH_2\\ |\\ C{:}NOH\end{matrix},$$

was prepared from 5 grams of the oxime and 3·2 grams of *m*-nitrobenzaldehyde by heating with alcohol and a few drops of ammonia in a sealed tube during four hours at 100°. On crystallising the product from acetone mixed with petroleum, it was obtained in minute, flat, transparent needles, melting at 215° with vigorous decomposition:

0·1923 gave 0·4051 CO_2 and 0·1117 H_2O. C = 57·45; H = 6·45.

$C_{18}H_{23}O_4N_5$ requires C = 57·91; H = 6·16 per cent.

A solution containing 0·1367 gram dissolved in 25 c.c. of chloroform gave α_D 1°23′ in a 2-dcm. tube, whence $[\alpha]_D$ 126·5°. The substance is insoluble in petroleum, dissolving sparingly in cold chloroform or boiling benzene, crystallising from the latter in silky needles; it is moderately soluble in hot methyl or ethyl alcohol, and in cold ethyl acetate, whilst cold acetone and glacial acetic acid dissolve it freely.



The *furfurylidene* compound, $C_8H_{14}<\begin{matrix}CH\cdot N(N{:}CH\cdot C_4H_3O)\cdot CO\cdot NH_2\\ |\\ C{:}NOH\end{matrix}$, obtained by heating 5 grams of the oxime with 2·5 grams of furfuraldehyde in absolute alcohol during three days under a reflux condenser, was crystallised several times from alcohol, and finally precipitated from chloroform by petroleum; it melts and decomposes at 225°:

0·1859 gave 28·4 c.c. of nitrogen at 20° and 770 mm. N = 17·71.

$C_{16}H_{22}O_3N_4$ requires N = 17·61 per cent.

A solution containing 0·3311 gram in 25 c.c. of chloroform gave α_D 3°12′ in a 2-dcm. tube, whence $[\alpha]_D$ 120·8°. The substance is insoluble in petroleum, and crystallises from boiling benzene in slender, transparent, prismatic needles; it is readily soluble in cold chloroform, ethyl acetate, or acetone, combining with the last-named medium. Ethyl alcohol deposits it in fern-like aggregates, and it crystallises from methyl alcohol in transparent, hexagonal prisms.

Oxime of Camphorylazoimide, $C_8H_{14}<\begin{matrix}CH\cdot N_3\\ |\\ C:NOH\end{matrix}$.

$$C_8H_{14}<\begin{matrix}CH\cdot N_3\\ |\\ C:NOH\end{matrix}$$

Forty grams of camphorylazoimide dissolved in 500 c.c. of absolute alcohol were treated during eight hours with 20 grams of hydroxylamine hydrochloride and 30 grams of anhydrous sodium acetate dissolved in water, then for a few hours with a further 10 grams of the hydrochloride and 15 grams of the acetate; the filtered liquid was evaporated and treated with water, but the product, even after the second treatment with hydroxylamine, solidified very slowly, and required to be recrystallised several times from dilute alcohol before the melting point remained constant. The oxime forms lustrous, silky needles melting at 84°:

0·1989 gave 0·4192 CO_2 and 0·1462 H_2O. C = 57·48; H = 8·16.
0·1153 ,, 27·6 c.c. of nitrogen at 23° and 770° mm. N = 27·34.
$C_{10}H_{16}ON_4$ requires C = 57·69; H = 7·70; N = 26·92 per cent.

Determinations of rotatory power were carried out in a 2-dcm. tube, 25 c.c. of solvent being employed in each case:

0·5046 gram in benzene gave α_D − 8°0′, whence $[\alpha]_D$ − 198·2°.
0·5037 ,, in absolute alcohol gave α_D − 6°27′, whence $[\alpha]_D$ − 160·1°.
0·5128 ,, in acetone gave α_D − 6°43′, whence $[\alpha]_D$ − 163·7°.
0·5230 ,, in chloroform gave α_D − 6°45′, whence $[\alpha]_D$ − 161·3°.

It dissolves very readily in petroleum or in cold alcohol, but is very sparingly soluble in boiling water, from which it crystallises in thread-like needles; it is odourless, and only very slightly volatile in steam. Compared with camphorylazoimide and camphoroxime, the substance is most inert. It does not yield a benzoyl derivative by the Schotten-Baumann method, and it is indifferent towards cold alcoholic potash; dilute sulphuric acid dissolves it slowly without eliminating hydroxylamine, and if the acid solution is boiled it becomes turbid, and a volatile oil, probably a nitrile, is formed, having a pungent odour of peppermint, again without production of hydroxylamine.

In working with camphorylazoimide we made many attempts, under varying conditions, to remove the nitrogen in the form of hydrazoic acid, but without success. The oxime, however, when boiled with alcoholic potash yields hydrazoic acid, which has been isolated as usual in the form of the silver salt; we have not identified the remaining products, having satisfied ourselves that the hoped-for structural isomeride of *iso*nitrosocamphor is not among them.

Royal College of Science, London,
South Kensington, S.W.

LXXXI.—*The Constituents of the Essential Oil of American Pennyroyal. Occurrence of a Dextro-Menthone.*

By MARMADUKE BARROWCLIFF.

THE essential oil obtained by distillation from the labiate plant *Hedeoma pulegioides* (Linné) Persoon, commonly known as American Pennyroyal, was first investigated by Kremers (*Proc. Amer. Pharm. Assoc.*, 1887, **35**, 546), who stated that it contained esters of formic, acetic, and *iso*heptoic acids, together with two compounds having the empirical formula $C_{10}H_{18}O$, which were designated "hedeomol." These compounds, which were separated by the fractional distillation of the hydrolysed oil, were found to boil respectively at 168—171° and 206—209°. In a subsequent communication (*Pharm. Rundschau*, 1891, **9**, 130), Kremers showed that both these compounds were ketones. From the fraction of the oil boiling at 168—171° he prepared a crystalline oxime melting at 41—43°, whilst the fraction boiling at 206—209° yielded an oxime melting at 52°, which he indicated might possibly be *l*-menthoxime. Somewhat later, Habhegger (*Amer. J. Pharm.*, 1893, **65**, 417) identified pulegone as a constituent of the oil.

The necessity having arisen for preparing a quantity of pulegone, for which the oil of hedeoma appeared to be a convenient source, it was deemed desirable to examine more completely the other constituents of this oil, and the results are embodied in the present communication.

EXPERIMENTAL.

The material employed for this investigation was obtained from Messrs. Fritzsche Brothers, New York, and possessed the characters of a genuine hedeoma oil. It had a density of 0·9297 at 15°/15°, an optical rotation at 22° of $+25°44'$ in a 1-dcm. tube, and was soluble in twice its volume of 70 per cent. alcohol. By a preliminary determination of the amount of free and combined acids, it was found that 20 grams of the oil required 0·064 gram NaOH to neutralise the free acids and 0·1025 gram NaOH to hydrolyse the esters present.

Treatment with Sodium Carbonate.—The entire amount of oil (2200 grams) was first shaken three times successively with a 10 per cent. solution of sodium carbonate. The combined alkaline liquids were extracted with ether to remove any suspended oil, then acidified with sulphuric acid, and distilled in steam. The distillate, which contained some oily drops, was extracted with ether, and the ethereal solution well washed with water, the washings being added to the aqueous distillate. From the acids remaining in the latter a barium salt was prepared, which gave the reactions of formic and butyric acids. The oily acids which had been extracted by ether were neutralised with potassium hydroxide, and subsequently converted into silver salts by fractional precipitation with a solution of silver nitrate. These were washed, dried, and analysed:

Fraction	I.	0·1837	of silver salt	gave	0·0707 Ag.	Ag = 38·4.
„	II.	0·1286	„	„	0·0514 Ag.	Ag = 39·9.
„	III.	0·2251	„	„	0·0918 Ag.	Ag = 40·7.
„	IV.	0·2205	„	„	0·0914 Ag.	Ag = 41·4.
„	V.	0·2329	„	„	0·0975 Ag.	Ag = 41·8.
„	VI.	0·1844	„	„	0·0786 Ag.	Ag = 42·6.

$C_{10}H_{19}O_2Ag$ requires Ag = 39·0 per cent.
$C_8H_{15}O_2Ag$ „ Ag = 43·0 „

The oily acids therefore appear to be a mixture of octoic and decylic acids. No indication was obtained of the presence of *iso*heptoic acid, which Kremers (*Proc. Amer. Pharm. Assoc.*, 1887, **35**, 546) considered to be a constituent of the oil.

Treatment with Potassium Hydroxide.—After the treatment with sodium carbonate the oil was extracted three times successively with a 5 per cent. solution of potassium hydroxide, then washed with water, and dried with anhydrous sodium sulphate. The combined alkaline liquids were extracted with ether to remove a small amount of suspended oil, then acidified with sulphuric acid, and again extracted with ether. This ethereal liquid was shaken with a solution of sodium carbonate, washed, dried, and the solvent removed, when a very small amount of a viscid oil was obtained which had a creosote-like odour and gave a brown coloration with ferric chloride. This substance was evidently a phenol, but an attempt to obtain a crystalline benzoyl derivative from it was unsuccessful.

Identification of Salicylic Acid.

The alkaline liquid obtained by shaking the above-mentioned ethereal liquid with a solution of sodium carbonate was acidified with sulphuric acid and extracted with ether. This ethereal liquid, after the removal of the solvent, yielded a small amount of a crystalline solid, which was brought on a porous plate to remove a little adhering oil, and then recrystallised from water, from which it separated in needles melting at 156°. It gave a violet coloration with ferric chloride:

0·1046 gave 0·2332 CO_2 and 0·0411 H_2O. C = 60·8; H = 4·4.

$C_7H_6O_3$ requires C = 60·9; H = 4·3 per cent.

This substance was thus identified as salicylic acid. As the original oil had previously been extracted with sodium carbonate, this acid could not have existed in it in a free state, and was probably present in the form of methyl salicylate, which had become hydrolysed in the process of isolation.

Preliminary Examination of the Terpenes.—In order to test for the presence of an olefinic or other unstable terpene, the oil which had previously been extracted with sodium carbonate and caustic alkali, as above described, was distilled under 60 mm. pressure, and the portion which passed over below 120° (about 50 c.c.) separately collected. This was again distilled under the same pressure, when it was resolved into the following fractions: below 105°, 105—120°; above 120°. The fraction boiling below 105°/60 mm. had the odour of pinene and a density of 0·8508 at 15°/15°, which indicated the absence of any olefinic terpene. The fraction 105—120°/60 mm. was specially tested for phellandrene, but with a negative result. All the above fractions were subsequently added to the main portion of the oil after the latter had been hydrolysed.

Isolation of Pulegone.

The entire portion of the oil boiling above 120°/60 mm. was treated with a solution of sodium bisulphite according to the method employed by Baeyer for the separation of pulegone from the oil of *Mentha Pulegium* (*Ber.*, 1895, **28**, 652), and the mixture actively shaken for ten days. This effected the separation of a large quantity of a crystalline bisulphite compound, which was removed by filtration and washed with alcohol and ether. The uncombined oil contained in the filtrate and washings was extracted with ether, and the ethereal solution dried with anhydrous sodium sulphate. After the removal of the ether the residual oil was rectified under 60 mm. pressure, when a small quantity of resinous matter remained in the flask. The further treatment of this portion of the oil is subsequently described.

The solid bisulphite compound and the aqueous filtrate therefrom, which had been freed from uncombined oil, were then separately decomposed by warming with a solution of potassium hydroxide, and the liberated ketone extracted with ether and dried. That obtained from the solid bisulphite compound distilled at 135—140°/65 mm. as a colourless oil, which acquired a slight yellow colour on standing, and amounted to 390 grams:

0·1027 gave 0·2966 CO_2 and 0·0979 H_2O. C = 78·8; H = 10·6.

$C_{10}H_{16}O$ requires C = 78·9; H = 10·5 per cent.

$d = 0·9377$ at 20°/20°; α_D +19°50′ in a 1-dcm. tube, whence $[\alpha]_D$ +21·15°.

A portion of this ketone was treated with semicarbazide hydrochloride and sodium acetate, when a semicarbazone was obtained which, after crystallisation from methyl alcohol, melted sharply at 171°, the melting point of pulegone semicarbazone.

The oil obtained by treating the aqueous bisulphite liquid with alkali likewise distilled at 135—140°/65 mm., and amounted to 140 grams. It had an optical rotation of +18°28′ in a 1-dcm. tube, and yielded a semicarbazone melting at 171°. It therefore also consisted of pulegone, and the somewhat lower rotatory power may be due to its having become partially racemised. The total quantity of pulegone obtained by the above treatment with bisulphite thus corresponds to 24·1 per cent. of the original oil.

Hydrolysis of the Oil.

The oil from which the pulegone had been removed as completely as possible by the above-described treatment with bisulphite was hydrolised by boiling it for two hours with a solution of 16 grams of potassium hydroxide in 400 c.c. of 90 per cent. alcohol, the mixture being frequently shaken. After removing the greater portion of the alcohol, a quantity of water was added, and the mixture extracted with ether, the ethereal solution being subsequently washed with water and dried with anhydrous sodium sulphate. After the removal of the ether the product was distilled under a pressure of 60 mm., when the greater portion passed over between 135° and 155°, a small quantity of resinous substance being left in the flask. The weight of the hydrolysed oil thus obtained was 1115 grams.

Fractional Distillation of the Oil.

The whole of the oil remaining from the foregoing treatment, to which was added the small portion that had been separated for the preliminary examination of the terpenes, was then subjected to repeated fractional distillation under the ordinary pressure, when the following fractions were finally collected: 155—165°, 165—170°, 170—180°, 180—190°, 190—200°, 200—207°, 207—212°, 212—217°, 217—224°, 224—240°, 240—250°, 250—260°, 260—270°, 270—280°, 280—290°, 290—300°, 300—310°.

Identification of Pinene.

Fraction 155—165°.—This was a colourless, mobile liquid and amounted to 7 grams:

0·1237 gave 0·3536 CO_2 and 0·1248 H_2O. C = 78·0; H = 11·2.

d 16·5°/16·5° = 0·8867; a_D −3°32′ in a 1-dcm. tube.

The characters of this fraction indicated that it consisted of a terpene, mixed with some of the oxygenated constituents of the oil. In order to remove the latter as completely as possible, it was washed several times with 70 per cent. alcohol, when a small amount of liquid remained which was sparingly soluble in this solvent. It then yielded a small quantity of a crystalline nitrosochloride, melting at 103—104°, from which the corresponding nitrolbenzylamine, melting at 122°, was prepared. The presence of a small amount of *l*-pinene in the oil was thus established.

Identification of 1-*Methyl*-3-cyclo*hexanone.*

Fraction 165—170°.—This was a colourless, limpid liquid having an agreeable odour. It distilled for the most part at 166—168° and amounted to 87 grams:

0·1337 gave 0·3780 CO_2 and 0·1324 H_2O. C = 77·1; H = 11·0.

d 16·5°/16·5° = 0·9006; α_D − 0°10′ in a 1-dcm. tube.

This fraction, although consisting chiefly of an oxygenated substance, evidently contained some pinene. Its solution in chloroform decolorised a considerable amount of bromine, hydrogen bromine being evolved.

On treatment with hydroxylamine an oxime was obtained which distilled at 130° under 33 mm. pressure, and then slowly solidified in fine needles melting at 41—43°. This melting point corresponds with that of an oxime obtained by Kremers (*Pharm. Rundschau*, 1891, 9, 130) from a fraction of hedeoma oil boiling at 168—171°, but which appears not to have been identified or further examined by him:

0·1073 gave 0·2585 CO_2 and 0·0985 H_2O. C = 65·7; H = 10·2.

$C_7H_{13}ON$ requires C = 66·1; H = 10·2 per cent.

A portion of the fraction was treated with semicarbazide hydrochloride and sodium acetate, when a semicarbazone was readily obtained. After crystallisation from alcohol it was obtained in glistening plates melting at 182—183°:

0·1164 gave 0·2420 CO_2 and 0·0919 H_2O. C = 56·7; H = 8·8.

$C_8H_{15}ON_3$ requires C = 56·8; H = 8·9 per cent.

Nine grams of the semicarbazone were decomposed with dilute sulphuric acid and the liberated ketone distilled in steam. The distillate was then extracted with ether, the ethereal solution dried, and the solvent removed, when a residue was obtained which distilled at 167—168° as a colourless, mobile oil:

0·1098 gave 0·3018 CO_2 and 0·1068 H_2O. C = 75·0; H = 10·8.

$C_7H_{12}O$ requires C = 75·0; H = 10·7 per cent.

d = 0·9154 at 20°/20°; α_D + 12°0′ in a 1-dcm. tube, whence $[\alpha]_D$ + 13·1°.

This ketone is thus seen to agree in its composition and characters with 1-methyl-3-*cyclo*hexanone (compare Aschan, *Chemie der alicyklischen Verbindungen,* 1905, p. 651), and it appears to be the first instance in which its occurrence in nature has been observed. Further confirmation of its identity was afforded by condensing a portion with benzaldehyde in the presence of a dilute solution of sodium hydroxide, when a dibenzylidene compound was obtained, which crystallised from alcohol in yellow needles melting at 125—126°.

By the treatment of the above fraction (b. p. 165—170°) with an excess of hydroxylamine hydrochloride and distillation of the product under diminished pressure, a small fraction was obtained which distilled below the boiling point of the oxime (130°/33 mm.). This, on redistillation at the ordinary pressure, boiled at 170—176°, had the odour of limonene, and an optical rotation of $-42°$ in a 1-dcm. tube. When treated with a slight excess of bromine, and the product crystallised from ethyl acetate, dipentene tetrabromide (m. p. 124°) was obtained. The mother liquors from the crystallisation of the latter compound yielded a small amount of limonene tetrabromide (m. p. 104°):

Fraction 170—180°.—This amounted to 7 grams:

0·1170 gave 0·3276 CO_2 and 0·1154 H_2O. C = 76·4; H = 10·9.
d 16·5°/16·5° = 0·9048; α_D + 2°4′ in a 1-dcm. tube.

This fraction was tested for cineol, but with a negative result. It was distilled twice over sodium, when the greater portion of the oxygenated substances was removed, and was then found to contain small amounts of dipentene and limonene, which were identified by means of their tetrabromo-derivatives:

Fraction 180—190°.—The amount of this fraction was 7 grams:

0·0984 gave 0·2748 CO_2 and 0·0981 H_2O. C = 76·2; H = 11·1.
d 16·5°/16·5° = 0·9051; α_D + 3°12′ in a 1-dcm. tube.

Fraction 190—200°.—This amounted to only 3 grams:

0·1075 gave 0·3039 CO_2 and 0·1082 H_2O. C = 77·1; H = 11·2.
d 16·5°/16·5° = 0·9023; α_D + 5°40′ in a 1-dcm. tube.

Fraction 200—207°.—This was the same in amount as the preceding fraction:

0·1047 gave 0·2966 CO_2 and 0·1055 H_2O. C = 77·2; H = 11·2.
d 16·5°/16·5° = 0·9031; α_D + 7°12′ in a 1-dcm. tube.

The three preceding fractions were too small in amount to admit of further examination. They evidently consisted of mixtures of the constituents of the fractions of lower and higher boiling point.

Fraction 207—212°.—The amount of this fraction was 65 grams:

0·1165 gave 0·3302 CO_2 and 0·1176 H_2O. C = 77·3; H = 11·2.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

d 20°/20° = 0·9048; α_D + 16°22′ in a 1-dcm. tube.

This fraction was examined after the composition of the following one had been determined, and was found to consist largely of the constituents of that fraction.

Fraction 212—217°.—This was by far the largest fraction obtained and amounted to 620 grams:

0·1349 gave 0·3849 CO_2 and 0·1358 H_2O. C = 77·8; H = 11·2.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

$C_{10}H_{16}O$,, C = 78·9; H = 10·5 ,,

d 20°/20° = 0·9121; α_D + 19°8′ in a 1-dcm. tube.

This fraction combined completely with hydroxylamine, yielding an oily oxime which deposited no solid, even on long standing. As there appeared to be still some pulegone present, 100 grams of the fraction were treated with sodium bisulphite solution in the manner previously described, when 8·5 grams of a bisulphite compound were obtained. This, when decomposed with a solution of potassium hydroxide, yielded an oil which, both by its boiling point and by its semicarbazone, was identified as pulegone.

Isolation of l-*Menthone and* d-iso*Menthone.*

Ten grams of the fraction (b. p. 212—217°) from which the further quantity of pulegone had been removed, were treated with semicarbazide hydrochloride and sodium acetate. The semicarbazone thus obtained was dissolved in hot absolute alcohol, in which the greater portion appeared to be very sparingly soluble. On cooling, a quantity (8·5 grams) of a substance separated in long, handsome needles which melted at 184—186°, and this melting point was not altered by further crystallisation. This substance corresponded in melting point with *l*-menthone semicarbazone, and a mixture of it with the semicarbazone from pure *l*-menthone (Kahlbaum) showed no diminution in melting point. The ketone was regenerated from it by distilling rapidly in steam with dilute sulphuric acid. The distillate was then extracted with ether, the ethereal solution dried with anhydrous sodium sulphate, and the solvent removed, when a liquid was obtained which distilled completely at 207—208°:

0·1320 gave 0·3768 CO_2 and 0·1370 H_2O. C = 77·8; H = 11·5.

$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

d = 0·8957 at 20°/20°; α_D − 10°8′ in a 1-dcm. tube, whence $[\alpha]_D$ − 11·3°.

This substance was evidently *l*-menthone, and the difference between its optical rotation and that of pure *l*-menthone may be attributed to its having become partially racemised by the action of the sulphuric acid during its liberation from the semicarbazone.

The oxime was prepared, and, after recrystallisation from alcohol, melted at 58—59°.

The mother liquors from the above-mentioned semicarbazone were concentrated, and the solid obtained from them fractionally crystallised from alcohol. A further small quantity of *l*-menthone semicarbazone was thus separated, and also 3·5 grams of a substance melting at 136—139°, which crystallised in hard masses of imperfectly formed cubes. The ketone regenerated from this was found to distil at 211—216°:

0·0954 gave 0·2730 CO_2 and 0·0975 H_2O. C = 78·0; H = 11·3.
d 20°/20° = 0·9148; α_D + 24°16′ in a 1-dcm. tube.

From the analytical figures and physical characters it appeared probable that this substance was a mixture of a strongly dextrorotatory ketone, $C_{10}H_{18}O$, with some pulegone.

The above-mentioned mother liquors also yielded about 3 grams of an uncrystallisable oil from which the ketone was regenerated. This distilled at 210—214° and had α_D + 31°36′ in a 1-dcm. tube:

0·1157 gave 0·3302 CO_2 and 0·1182 H_2O. C = 77·8; H = 11·3.
$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

It was evident that this substance also consisted largely of a ketone of the formula $C_{10}H_{18}O$.

It therefore seemed probable that if the pulegone still contained in the fraction of oil boiling at 212—217° could be removed, the semicarbazone of the dextrorotatory ketone might be isolated in a state of purity. With this object in view 100 grams of the respective fraction were warmed with a mixture of 33 grams of potassium dichromate and 11 grams of sulphuric acid in 250 c.c. of water, the mixture being frequently shaken. The unchanged ketone was then distilled in steam and extracted, when a liquid was obtained which distilled at 211—213°, and had α_D + 15°36′ in a 1-dcm. tube. Fifteen grams of this liquid were converted into semicarbazones, which were fractionally crystallised from alcohol, when 12·5 grams of *l*-menthone semicarbazone were obtained. The remainder consisted almost entirely of a compound which, after drying at 100°, melted at 125—126°, only a very small amount of the product being uncrystallisable.

The semicarbazone melting at 125—126° was decomposed with dilute sulphuric acid and the liberated ketone distilled as rapidly as possible in steam. It was then extracted, and found to boil constantly at 209—210°:

0·1187 gave 0·3392 CO_2 and 0·1247 H_2O. C = 77·9 ; H = 11·7.

$C_{10}H_{18}O$ requires C = 77·9 ; H = 11·7 per cent.

$d = 0{\cdot}8961$ at 20°/20° ; a_D + 43°36′ in a 1-dcm. tube, whence $[a]_D$ + 48·6°.

It seemed likely that this ketone was a stereoisomeride of *l*-menthone, as the physical constants of the two compounds, with the exception of the optical rotation, were practically the same. Its oxime is an oil.

Beckmann (*Annalen*, 1889, **250**, 322) has shown that when *l*-menthone ($[a]_D$ about − 28°) is treated with 90 per cent. sulphuric acid, a product is obtained which possesses a rotatory power of about $[a]_D$ + 28°. It appeared probable that this change was due to the racemisation of one of the two asymmetric carbon atoms contained in the ketone, and that, if this were the case, the resulting mixture might be separated into its components by the fractional crystallisation of the semicarbazones obtained from it. In order to ascertain whether this could be accomplished, the following experiment was conducted.

Fifteen grams of *l*-menthone (Kahlbaum) having a rotation of $[a]_D$ − 28·0° were inverted according to the method employed by Beckmann (*loc. cit.*), when a product was obtained which had a rotation of $[a]_D$ + 22°. Twelve grams of this were converted into the semicarbazones, which were fractionally crystallised from alcohol. A quantity (9·6 grams) of a compound melting at 184—186° was thus obtained, which was shown to be *l*-menthone semicarbazone, both by comparison with the latter and by the characters of the regenerated ketone. The mother liquors yielded a substance melting at 126—127° * which crystallised in imperfectly-formed cubes. This was found to be identical with the above-described semicarbazone melting at 125—126°. The ketone regenerated from it was found to boil at 208—209°, had $d = 0{\cdot}8988$ at 20°/20°, and a_D + 42°20′ in a 1-dcm. tube, whence $[a]_D$ + 47·1°. This menthone thus possesses the highest dextrorotatory power that has as yet been observed.

Beckmann (*J. pr. Chem.*, 1897, **55**, 18), by oxidising *iso*menthol with chromic acid, obtained menthones varying in optical rotation from $[a]_D$ + 30° to $[a]_D$ + 35°, values considerably lower than that recorded above.

The amount of *l*-menthone semicarbazone obtained from the above-described "inverted menthone" ($[a]_D$ + 22°) indicates that it must have contained at least 60 per cent. of *l*-menthone ($[a]_D$ − 28°). The specific rotation of the dextrorotatory constituent of this mixture, calculated from these figures, would therefore be $[a]_D$ + 97°. It is thus probable that the above-described dextrorotatory menthone did not possess its full degree of optical activity, and that the difference between the calculated value ($[\alpha]_D$ +97°) and the figures actually obtained ($[\alpha]_D$ +47·1° to +48·6°) may be attributed to racemisation having taken place during the liberation of the ketone from its semicarbazone.

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* The mother liquors from this second semicarbazone yielded a very small quantity of a substance which crystallised in fine needles melting at 161—163°. The nature of this compound has not been determined.

Since the menthone molecule contains two asymmetric carbon atoms, ordinary *l*-menthone must be represented by either the configuration – – or – +. On treatment with sulphuric acid, one of these asymmetric carbon atoms, without doubt the one situated in the α-position to the keto-group, undergoes racemisation, and it has been shown that the resulting mixture consists of *l*-menthone, together with a second menthone possessing a rotatory power of opposite sign but of greater value than that of the former ketone. It follows from this that ordinary *l*-menthone must be represented by the second configuration, namely, – +, and that on treatment with sulphuric acid the carbon atom possessing a lævorotatory power undergoes racemisation. The *d*-menthone contained in hedeoma oil, and also in Beckmann's "dextro-menthone" (*Annalen*, 1889, **250**, 322), must therefore be represented by the configuration + +. As this ketone is not the optical antipode of *l*-menthone, it would seem advisable to denote it by some distinctive name, such as *d*-*iso*menthone.* The two other possible menthones, possessing the configurations – – and + – respectively, both of which are apparently at present unknown, would then be designated respectively as *l*-*iso*menthone and *d*-menthone.

Fraction 217—224°.—The amount of this fraction was 43 grams:

0·1616 gave 0·4638 CO_2 and 0·1565 H_2O. C = 78·3; H = 10·8.
d 20°/20° = 0·9257; α_D +23°0′ in a 1-dcm. tube.

A portion of this fraction was treated with semicarbazide and the resulting semicarbazones fractionally crystallised, when it was found to consist of the constituents of the preceding fraction, but containing a larger proportion of pulegone than the latter.

Fraction 220—240°.—This amounted to 10 grams:

0·1083 gave 0·3125 CO_2 and 0·1052 H_2O. C = 78·7; H = 10·8.
d 20°/20° = 0·9270; α_D +12°4′ in a 1-dcm. tube.

This consisted of pulegone and the constituents of the fractions of higher boiling point.

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* This nomenclature is in accordance with that adopted by Aschan (*Chemie der alicyklischen Verbindungen*, 1905, p. 657), who designated the "*d*-menthone" of Beckmann as *d*-*iso*menthone, but recognised that this is a mixture of *l*-menthone and a hitherto unknown dextrorotatory menthone which, when isolated, would properly receive the name *d*-*iso*menthone.

Fraction 240—250°.—The amount of this fraction was only 3 grams:

0·1008 gave 0·2935 CO_2 and 0·0978 H_2O. C = 79·8; H = 10·8.
d 20°/20° = 0·9296; α_D + 4°56′ in a 1-dcm. tube.

Fraction 250—260°.—This amounted to 3 grams:

0·1173 gave 0·3415 CO_2 and 0·1145 H_2O. C = 79·4; H = 10·8.
d 20°/20° = 0·9302; α_D − 0°24′ in a 1-dcm. tube.

Fraction 260—270°.—This amounted to 3 grams:

0·1100 gave 0·3163 CO_2 and 0·1067 H_2O. C = 78·4; H = 10·8.
d 20°/20° = 0·9322; α_D + 0°12′ in a 1-dcm. tube.

Fraction 270—280°.—This amounted to 3 grams:

0·1289 gave 0·3717 CO_2 and 0·1245 H_2O. C = 78·6; H = 10·7.
d 20°/20° = 0·9385; α_D + 1°56′ in a 1-dcm. tube.

Fraction 280—290°.—This amounted to 3 grams:

0·1090 gave 0·3121 CO_2 and 0·1055 H_2O. C = 78·1; H = 10·7.
d 20°/20° = 0·9375; α_D + 4°56′ in a 1-dcm. tube.

As the five preceding fractions were all so very small in amount, they were not further examined.

Fraction 290—300°.—The amount of this fraction was 8 grams:

0·1099 gave 0·3187 CO_2 and 0·1092 H_2O. C = 79·1; H = 11·0.
d 20°/20° = 0·9307; α_D + 9°32′ in a 1-dcm. tube.

The characters of this fraction indicated it to consist of a mixture of the constituents of the preceding and the following fractions.

Fraction 300—310°.—The amount of this fraction was 7 grams:

0·1150 gave 0·3375 CO_2 and 0·1151 H_2O. C = 80·0; H = 11·1.
$C_{15}H_{26}O$ requires C = 81·1; H = 11·7 per cent.
d 20°/20° = 0·9259; $[\alpha]_D$ + 12°48′ in a 1-dcm. tube.

The analysis and boiling point of this fraction indicated that it might contain a sesquiterpene alcohol, and as it was impossible to obtain the latter in a state of purity, it was deemed of interest to prepare the corresponding sesquiterpene from it. The entire fraction was accordingly distilled several times over phosphoric oxide, and then twice over metallic sodium under 60 mm. pressure, when it finally passed over between 160° and 170°. Under the ordinary pressure it distilled between 270° and 280°:

0·0890 gave 0·2872 CO_2 and 0·0916 H_2O. C = 88·0; H = 11·4.
$C_{15}H_{24}$ requires C = 88·2; H = 11·8 per cent.
d 20°/20° = 0·8981; α_D + 1°4′ in a 1-dcm. tube; n_D^{20} = 1·5001.

Molecular refraction, 66·80.

The value obtained for the molecular refraction indicates that this substance belongs to the group of bicyclic sesquiterpenes with two ethylenic linkings. By the production of this sesquiterpene indirect evidence is afforded of the presence of a small amount of a sesquiterpene alcohol in hedeoma oil.

Acids Obtained by the Hydrolysis of the Oil.

The strongly alkaline aqueous liquid which was separated from the hydrolysed oil, and from which all adhering oil had been removed by extraction with ether, as previously described, was concentrated to a small bulk, then acidified with sulphuric acid, and distilled with steam. The distillate contained a small amount of an oily liquid, which was extracted with ether, the ethereal solution being subsequently washed with water and dried. The acids remaining in the aqueous distillate were converted into their barium salts and found to be formic and acetic acids. After removing the solvent from the ethereal solution of volatile acids, the latter were converted into the sodium salts, from which, by the addition of silver nitrate, the corresponding silver salts were precipitated in five fractions. These were washed, dried, and analysed:

Fraction I. 0·2130 of silver salt gave 0·0827 Ag. Ag = 38·82.
„ II. 0·1154 „ „ 0·0455 Ag. Ag = 39·42.
„ III. 0·1214 „ „ 0·0493 Ag. Ag = 40·60.
„ IV. 0·1048 „ „ 0·0435 Ag. Ag = 41·50.
„ V. 0·1179 „ „ 0·0500 Ag. Ag = 42·40.
$C_{10}H_{19}O_2Ag$ requires Ag = 39·0 per cent.
$C_8H_{15}O_2Ag$ „ Ag = 43·0 „

These volatile acids would thus appear to consist of a mixture of octoic and decylic acids.

After the distillation of the volatile acids there remained in the distilling flask about 5 grams of an oily liquid which was not volatile in steam. This was extracted with ether, and the ethereal liquid subsequently shaken with a solution of sodium carbonate. The aqueous alkaline liquid was then acidified, when a viscous, brown oil was precipitated, which was extracted with ether, and, after the removal of the solvent, distilled under 20 mm. pressure. The main portion passed over at 180—240° as a viscid, pale brown oil, which, after standing for some weeks, deposited a fatty-looking solid substance. This was separated by filtration, brought on a porous plate to remove a little adhering oil, and then crystallised from ethyl acetate, from which it separated in needles melting at 83—85°:

0·1072 gave 0·2136 CO_2 and 0·0762 H_2O. C = 54·3; H = 7·9.
$C_8H_{14}O_4$ requires C = 55·4; H = 8·0 per cent.

From the ammonium salt of this acid the silver salt was prepared and analysed:

0·0896 of silver salt gave 0·0491 Ag. Ag = 54·8.

$C_8H_{12}O_4Ag_2$ requires Ag = 55·6 per cent.

These analytical figures render it probable that this crystalline substance is a dibasic acid of the formula $C_8H_{14}O_4$.

Summary.

From the results of this investigation the essential oil of *Hedeoma pulegioides* is seen to contain the following substances:

1. An undetermined phenol, in very small amount.
2. *l*-Pinene
3. *l*-Limonene } in small amount.
4. Dipentene
5. 1-Methyl-3-*cyclo*hexanone, about 8 per cent.
6. Pulegone, about 30 per cent.
7. *l*-Menthone } about 50 per cent.
8. *d*-iso*Menthone*
9. A sesquiterpene alcohol, about 2 per cent.
10. An ester of salicylic acid, probably methyl salicylate.
11. Esters of formic, acetic, octoic, and decylic acids, together with an ester of a dibasic acid of the probable formula $C_8H_{14}O_4$.
12. Formic, butyric, octoic, and decylic acids in the free state.

All the above-mentioned esters and acids are present only in small amount.

The author desires to express his warmest thanks to Dr. F. B. Power, both for the suggestion of this investigation, and for the kind advice and assistance he has afforded throughout the course of it.

The Wellcome Chemical Research Laboratories,
London, E.C.

LXXXII.—*The Constitution of Homoeriodictyol.—A Crystalline Substance from Eriodictyon Leaves.*

By Frederick Belding Power and Frank Tutin.

At the meeting of the American Pharmaceutical Association held at Indianapolis, Ind., in September, 1906, a paper was communicated by the authors, entitled "Chemical Examination of Eriodictyon" (compare *Pharm. J.*, 1906, **77**, 381, and Abstr., 1906, **90**, ii, 885). The material used for this investigation consisted of the leaves of *Eriodictyon californicum* (Hooker and Arnott), Greene (syn. *E. glutinosum*, Benth.), which had been specially collected for us in California.

In the above-mentioned communication it was shown that the leaves of eriodictyon contain, besides a small amount of essential oil, a considerable amount of glucose, resins, and other amorphous substances, the hydrocarbons triacontane (m. p. 65·2°) and pentatriacontane (m. p. 74·5—75°), together with formic, acetic, butyric, cerotic, and other acids, both in the free state and as glycerides, and a very small amount of a phytosterol (m. p. 136—137°). In addition to these, three new crystalline substances of a phenolic nature were isolated and described, namely:

1. A substance crystallising in fawn-coloured plates, melting at 267°, and possessing the formula $C_{15}H_{12}O_6$, which was designated *eriodictyol*.

2. A substance crystallising in pale yellow plates, melting at 223°, and possessing the formula $C_{16}H_{14}O_6$. As this substance was apparently a homologue of the preceding one, differing by the increment of CH_2, it was designated *homoeriodictyol*.

3. A very small quantity of a substance crystallising in minute, bright yellow spangles, and possessing the formula $C_{16}H_{12}O_6$.*

The amount of this last-mentioned substance present in the leaves (0·014 per cent.) was too small to permit of its further examination, and hence no name was given to it. Homoeriodictyol and eriodictyol, however, which occur to the extent of about 3 and 0·23 per cent. respectively of the weight of dried leaves, have now been further investigated, and the results obtained are embodied in the present communication.

Homoeriodictyol is isomeric with hesperitin, and its melting point (223°) is but three degrees lower than that recorded for the latter compound. It is also similar to hesperitin in most of its properties, and gives the same reaction as the latter compound when treated with sodium amalgam (Beilstein's *Handbuch*, Bd. III., 594). It was shown, however, not to be identical with hesperitin by the fact that its sodium derivative possesses the normal formula $C_{16}H_{13}O_6Na$, whereas sodium hesperitin has a composition agreeing with the formula

$$C_{16}H_{13}O_6Na,C_{16}H_{14}O_6$$

(Perkin, Trans., 1898, **73**, 1037). It was therefore concluded that homoeriodictyol possessed a constitution analogous to that of hesperitin to which Tiemann and Will (*Ber.*, 1881, **14**, 970) assigned the following formula:

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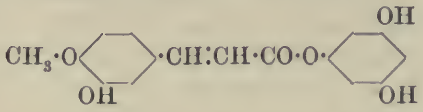
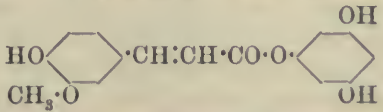
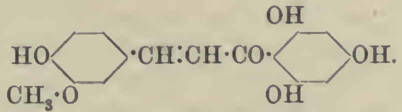
* In Abstr., 1906, **90**, ii, 885, the formula of this substance is incorrectly given as "$C_{16}H_{41}O_6(C_{16}H_{14}O_6?)$."



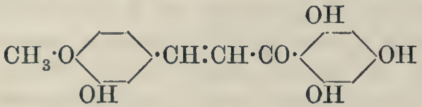
In view of this conclusion, homoeriodictyol has been submitted to the action of aqueous potassium hydroxide under the same conditions as were employed by Tiemann and Will (*loc. cit.*) for the hydrolysis of hesperitin, and it has been found that it undergoes hydrolysis in a manner analogous to that exhibited by the latter compound. The products yielded by the hydrolysis of homoeriodictyol are phloroglucinol and ferulic acid (4-hydroxy-3-methoxycinnamic acid), whilst hesperitin gives the same phenol together with *iso*ferulic acid (3-hydroxy-4-methoxycinnamic acid). On fusion with potash, homoeriodictyol, like hesperitin, readily gives protocatechuic acid. It would appear from these results that homoeriodictyol differs from hesperitin only in the position of the methylated hydroxyl group and that it possesses a constitution represented by the following formula:



If this were the case, homoeriodictyol would contain three hydroxyl groups and should give a triacetyl derivative. Acetylhomoeriodictyol (m. p. 154°) was therefore prepared, but on examining this compound it was found to contain four acetyl groups. Homoeriodictyol cannot therefore be represented by the above formula. The only alternative is that it possesses a ketonic structure, analogous to that of phloretin (*Ber.*, 1895, **28**, 1393), and consequently must possess the following constitution:



From a consideration of these facts it would appear that homoeriodictyol is not so closely related to hesperitin as was at first supposed, provided that the latter compound is correctly represented by the ester structure assigned to it by Tiemann and Will. The chief evidence in support of this ester structure for hesperitin appears to be that deduced by A. G. Perkin (*loc. cit.*), who obtained from the latter a triacetyl derivative. On the other hand, if hesperitin is a true ester it is difficult to see why it should yield phloroglucinol and *iso*ferulic acid when hydrolysed by boiling with concentrated alkalis, and that when heated with more dilute alkali only amorphous colouring matters should be produced (compare Tiemann and Will, *loc. cit.*, p. 953). It was, moreover, shown by Perkin that when acetylhesperitin is hydrolysed by means of sulphuric acid it gives a quantitative yield of hesperitin, none of the latter undergoing hydrolysis, and this behaviour would not be expected were hesperitin itself an ester. In view of these considerations it is most probable that hesperitin also possesses the ketonic structure, notwithstanding the fact that no tetra-acetyl derivative appears as yet to have been obtained from it. If this should prove to be the case, hesperitin would have the following constitution:



It will be seen that this formula for hesperitin differs from that assigned to homoeriodictyol only in the position of the methoxy-group.

The fact that the empirical formula of eriodictyol ($C_{15}H_{12}O_6$) differs from that of homoeriodictyol ($C_{16}H_{14}O_6$) by the elements CH_2, and that these two substances occur together in the plant, led to the conclusion that the latter compound might be a monomethyl ether of the former. This view receives support from a comparison of their properties and also from the fact that eriodictyol contains no methoxyl group, whilst it has been shown that homoeriodictyol contains one such group.

By the action of acetic anhydride on eriodictyol two compounds have been obtained. One of these melts at 137° and yielded results on analysis which indicate that it contains either four or five acetyl groups, whilst the other melts at 195—196°. The latter compound is obtained by the more prolonged action of the anhydride, and is possibly formed by the elimination of a molecule of water from the acetyl derivative melting at 137° (compare Ciamician and Silber, *Ber.*, 1895, **28**, 1395). The amount of eriodictyol at our disposal was insufficient to permit of its constitution being definitely ascertained.

Since the publication of abstracts of our paper (*loc. cit.*) on the "Chemical Examination of Eriodictyon" * a communication by Mossler has appeared, entitled: "*Ueber die chemische Untersuchung von Eriodictyon glutinosum*" (*Annalen*, 1907, **351**, 233). The author of this paper has isolated from eriodictyon leaves a substance of the formula $C_{16}H_{14}O_6$ (m. p. 214—215°) and proposes to designate it "eriodyctionon." This substance is evidently identical with the compound which the present authors had previously described and designated *homoeriodictyol*, although it is stated to have a melting point eight degrees lower than that of homoeriodictyol. The observations of Mossler respecting the presence in homoeriodictyol of one methoxyl and four hydroxyl groups are in agreement with the results recorded in the present paper, but we are unable to confirm his statement regarding the formation of an oxime from homoeriodictyol and its acetyl derivative respectively. On treating acetylhomoeriodictyol with hydroxylamine or with semicarbazide, hydrolysis resulted, the product in both cases being readily soluble in a cold dilute solution of sodium carbonate. Homoeriodictyol, after treatment with hydroxylamine, was recovered unchanged.

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* The full paper will appear in the *Proceedings of the American Pharmaceutical Association*, 1906.

It was finally stated by Mossler (*loc. cit.*, p. 253) that the results obtained by him did not permit of forming a conclusive opinion respecting the substance of the composition $C_{16}H_{14}O_6$, which he had isolated from eriodictyon leaves.

EXPERIMENTAL.

The method by which eriodictyol and homoeriodictyol were isolated from the leaves of *Eriodictyon californicum* was described in detail in the previous communication (*loc. cit.*), and was briefly as follows. The concentrated alcoholic extract of the leaves was distilled in steam for the removal of the volatile constituents, after which the aqueous liquid in the distillation flask was separated from the large cake of resins, and extracted with ether. On shaking this ethereal extract with a solution of sodium carbonate an alkaline aqueous liquid was obtained, which contained a crystalline precipitate of sodium homoeriodictyol. This substance was collected, purified by recrystallisation from hot water, decomposed by acetic acid, and the homoeriodictyol thus obtained recrystallised from 70 per cent. acetic acid. The original filtrate from the sodium homoeriodictyol, when acidified and extracted with ether, yielded eriodictyol, which was obtained pure by recrystallisation from alcohol, and subsequently from 70 per cent. acetic acid.

The resins which remained in the distilling flask were extracted with light petroleum and subsequently with ether, and on shaking the ethereal liquid thus obtained with a solution of sodium carbonate a further and larger quantity of sodium homoeriodictyol separated.

Homoeriodictyol, $C_{16}H_{14}O_6$, is moderately soluble in alcohol and in acetic acid, sparingly so in ethyl acetate, and nearly insoluble in water; it does not dissolve in either chloroform or benzene. When crystallised from 70 per cent. acetic acid it is obtained in handsome, pale yellow plates, which melt at 223°, and possess a slightly sweetish taste. If to a dilute alcoholic solution of homoeriodictyol a drop of ferric chloride solution is added, an intense reddish-brown colour is produced.

An estimation of the methoxyl groups present in homoeriodictyol by means of Perkin's modification of Zeisel's method gave the following result:

0·2656 gave 0·2032 AgI. MeO = 10·1.

$C_{15}H_{11}O_5 \cdot OMe$ requires MeO = 10·3 per cent.

It is thus evident that homoeriodictyol contains one methoxyl group.

Hydrolysis of Homoeriodictyol. Formation of Phloroglucinol and Ferulic Acid.

Six grams of homoeriodictyol were dissolved in a solution of 18 grams of potassium hydroxide in 60 c.c. of water, and the mixture, which rapidly became very dark in colour, boiled for three hours in a flask attached to a reflux condenser. The liquid was allowed to cool, and then acidified with hydrochloric acid, when a quantity of tarry matter separated. As it was probable that this precipitate contained unchanged homoeriodictyol, an excess of calcium carbonate was added, the mixture heated for half an hour, and then filtered. The filtrate, which was very brown in colour, did not become decolorised when boiled with animal charcoal. Sodium carbonate solution was therefore gradually added to the hot liquid, when the precipitate of calcium carbonate which was formed carried down with it the greater part of the colouring matter, and was removed by filtration. The filtrate was concentrated somewhat under diminished pressure, then repeatedly extracted with ether, and the ethereal liquid, after being washed with water and dried with calcium chloride, yielded on evaporation a syrupy residue, which, on the addition of a little water, instantly became crystalline. This crystalline substance possessed a strong vanilla-like odour, and its aqueous solution gave a dark violet colour on the addition of a drop of a solution of ferric chloride. It was recrystallised from water, when it separated in plates which possessed a somewhat brown colour, and were associated with a small amount of a viscid substance, but was obtained pure by crystallisation from a little anhydrous ethyl acetate. This substance, when separated from its aqueous solution, evidently contained water of crystallisation, but, when crystallised from dry ethyl acetate, was obtained in the anhydrous state. When rapidly heated it melted at about 218°:

0·0778 gave 0·1622 CO_2 and 0·0344 H_2O. C = 56·9 ; H = 4·9.

$C_6H_6O_3$ requires C = 57·1 ; H = 4·8 per cent.

This product of the hydrolysis of homoeriodictyol was thus identified as phloroglucinol, and the viscid substance originally associated with it, which possessed the vanilla-like odour, doubtless contained vanillin, as this compound would be produced by the oxidation of the ferulic acid which was subsequently isolated.

The aqueous liquid, from which the phloroglucinol had been removed by means of ether, was acidified with hydrochloric acid, when an acid of a tarry nature separated. This mixture was then shaken with a considerable volume of ether, when a quantity of a liquid tarry substance did not dissolve, but remained mixed with the ethereal liquid. The aqueous liquid was therefore separated, and the ethereal solution shaken with animal charcoal and filtered. On evaporating the filtrate, a crystalline residue was obtained, which was dissolved in hot ethyl acetate, when, on cooling, it separated in almost colourless needles which melted at 170°. A dilute aqueous solution of this acid gave with ferric chloride a dark red precipitate. The acid was analysed with the following result:

0·1103 gave 0·2508 CO_2 and 0·0517 H_2O. $C = 62·0$; $H = 5·2$.

$C_{10}H_{10}O_4$ requires $C = 61·9$; $H = 5·2$ per cent.

The properties of this substance agree with those of ferulic acid (4-hydroxy-3-methoxycinnamic acid), but for the purpose of confirming its identity with the latter a portion of it was methylated by means of sodium and methyl iodide, when 3 : 4-dimethoxycinnamic acid (m. p. 180°) and its methyl ester (m. p. 64°) were obtained.

Fusion of Homoeriodictyol with Potassium Hydroxide.—Two grams of homoeriodictyol were gradually added to a fused mixture of 20 grams of potassium hydroxide and a little water, the temperature of which was about 120°. A considerable amount of gas was evolved and the melt at first assumed a red colour, but when the temperature reached 190° the mass became colourless and tranquil. It was then dissolved in water, acidified with sulphuric acid, and extracted with ether, when an acid was obtained which crystallised from water in needles melting at 192°. This substance was evidently protocatechuic acid, as it gave with ferric chloride the colour reaction characteristic of this compound.

Tetra-acetylhomoeriodictyol, $C_{16}H_{10}O_6(CO·CH_3)_4$.

Two grams of homoeriodictyol were dissolved in 10 grams of acetic anhydride and 1 gram of fused sodium acetate added. After boiling the mixture for four hours it was shaken with water until the greater part of the anhydride was decomposed. Ether was then added, and the mixture again shaken vigorously, when the acetylated product, which had not become solid, was dissolved by the ether, from which it separated almost immediately in a crystalline state. The crystalline acetyl derivative was collected on a filter, washed, dried, and recrystallised from ethyl acetate, when it readily separated in slightly yellow needles which melted at 154°. On concentrating the mother liquors from this acetyl derivative, a substance separated which appeared to be not quite homogeneous, but no compound other than the acetylhomoeriodictyol melting at 154° could be isolated, nor was the melting point of this acetyl derivative altered by further crystallisation:

0·1239 gave 0·2794 CO_2 and 0·0524 H_2O. C = 61·5; H = 4·7.
$C_{16}H_{11}O_6(CO{\cdot}CH_3)_3$ requires C = 61·7; H = 4·7 per cent.
$C_{16}H_{10}O_6(CO{\cdot}CH_3)_4$ „ C = 61·3; H = 4·7 „

The acetyl groups present in acetylhomoeriodictyol were estimated as follows. A weighed quantity of the substance was hydrolysed by heating with a solution of potassium hydroxide, after which the liquid was acidified with sulphuric acid, and distilled from a double-necked flask until acid ceased to pass over:

0·3180 gave an amount of acetic acid equivalent to 0·1072 NaOH. $CH_3{\cdot}CO = 36{\cdot}2$.
0·2964 gave an amount of acetic acid equivalent to 0·1016 NaOH. $CH_3{\cdot}CO = 36{\cdot}8$.
$C_{16}H_{11}O_6(CO{\cdot}CH_3)_3$ requires $CH_3{\cdot}CO = 30{\cdot}1$ per cent.
$C_{16}H_{10}O_6(CO{\cdot}CH_3)_4$ „ $CH_3{\cdot}CO = 36{\cdot}6$ „

In view of the statement of Mossler (*loc. cit.*) that acetylhomoeriodictyol affords an oxime, the following experiments were conducted. Half a gram of acetylhomoeriodictyol was dissolved in alcohol, and an aqueous solution of 0·5 gram of hydroxylamine hydrochloride and 0·9 gram of sodium acetate added. The mixture, which rapidly became bright yellow, was allowed to stand overnight, when, on the addition of water, a yellow, viscid product separated. This contained no nitrogen, and was completely soluble in a dilute solution of sodium carbonate. An analogous experiment was conducted with the use of semicarbazide hydrochloride, and a similar result was obtained. In order to ascertain whether hydroxylamine would react with homoeriodictyol itself, 1 gram of the latter substance was dissolved in alcohol and a concentrated aqueous solution of 0·47 gram of hydroxylamine hydrochloride added. To this a solution of 0·15 gram of sodium in ethyl alcohol was then added, the mixture warmed, and allowed to stand overnight, after which it was mixed with a large volume of water. A substance was thus precipitated, which was collected on a filter and crystallised from ethyl acetate, in which it dissolved only sparingly. It was then found to melt at 223°, and evidently consisted of unchanged homoeriodictyol.

Several experiments were made with the object of ascertaining whether a completely methylated homoeriodictyol could be obtained, but it was found that the desired product was not readily formed. A *monomethylhomoeriodictyol* was, however, prepared in the following manner. A quantity of sodium homoeriodictyol was heated in a water-bath with an excess of methyl alcohol and methyl iodide, when the solid gradually passed into solution. After the heating had been continued for about three hours, water was added to the mixture, when a yellow substance was precipitated. This substance would not crystallise from anhydrous solvents, but when dissolved in a mixture of ether and 90 per cent. alcohol, and the solution allowed to evaporate spontaneously, it separated in aggregates of pale yellow leaflets which melted at about 80°. As thus obtained it evidently contained water of crystallisation, for, when heated at 100°, the fused substance gradually solidified, and was then found to melt at 138—139°:

0·1146, on heating at 105°, lost 0·0062 H_2O. $H_2O = 5·4$.

0·1084, dried at 105°, gave 0·2569 CO_2 and 0·0503 H_2O. $C = 64·6$; $H = 5·2$.

$C_{17}H_{16}O_6,H_2O$ requires $H_2O = 5·4$ per cent.

$C_{17}H_{16}O_6$ requires $C = 64·6$; $H = 5·1$ „

Eriodictyol, $C_{15}H_{12}O_6$.

Eriodictyol crystallises in fawn-coloured plates which melt at 267°. It is moderately soluble in hot alcohol and in acetic acid, very sparingly so in boiling water, and insoluble, or very sparingly soluble, in the other usual organic solvents. The fixed alkalis and alkaline carbonates readily dissolve it, yielding at first almost colourless solutions, which, however, rapidly absorb oxygen and assume a deep brown colour. It was ascertained, by means of Perkin's modification of Zeisel's method, that eriodictyol contains no methoxyl group.

Action of Acetic Anhydride on Eriodictyol.—A small quantity of eriodictyol was dissolved in a large excess of hot acetic anhydride and the mixture boiled for six hours. The greater part of the anhydride was then removed by distillation and a small quantity of alcohol added, when, after standing for some time, a solid substance separated. This was collected, and crystallised from ethyl acetate, when it was obtained in small tufts of minute, nearly colourless needles which melted at 195—196°. In another experiment 1 gram of eriodictyol was boiled for two hours with ten times its weight of acetic anhydride and 1 gram of anhydrous sodium acetate, at the end of which time water was added and the mixture shaken until the anhydride was decomposed. The product, which had not solidified, was then extracted with ether, the ethereal liquid being washed with a solution of sodium carbonate and subsequently with water. On removing the greater portion of the ether, a solid substance separated in the form of almost colourless prisms. This substance was collected on a filter and recrystallised from ethyl acetate, when it was observed to be not quite homogeneous. After two recrystallisations, however, it was obtained pure, and was then found to melt at 137°:

0·0970 gave 0·2146 CO_2 and 0·0405 H_2O. C = 60·3; H = 4·6.

$C_{15}H_8O_6(CO{\cdot}CH_3)_4$ requires C = 60·5; H = 4·4 per cent.

$C_{15}H_7O_6(CO{\cdot}CH_3)_5$,, C = 60·2; H = 4·4 ,,

The mother liquors from this acetyl derivative yielded a small quantity of a substance which crystallised in tufts of white needles melting at 195—196°, and was identical with the compound melting at this temperature which had previously been obtained by the more prolonged action of acetic anhydride on eriodictyol. The amount of eriodictyol available did not permit of the further examination of these acetyl derivatives.

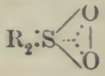
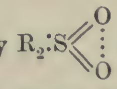
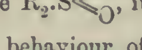
THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

LXXXIII.—*Contributions to the Chemistry of Oxygen Compounds. II. The Compounds of Cineol, Diphenylsulphoxide, Nitroso-derivatives, and the Carbamides with Acids and Salts.*

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

IN Part I (Trans., 1906, **89**, 262) we have shown that the various tri-alkyl phosphine oxides form compounds with acids and with metallic salts and can replace the ether in a "Grignard" reagent.

A variation in character of the substituent R in R_3PO has little or no effect on the capacity of these oxides to form so-called molecular compounds. In order to throw some light on the influence (if any) of the phosphorus atom on the formation of these compounds we have investigated the capacity of numerous other substances to combine with acids and metallic salts.

Cineol is a compound which possesses in a marked degree the property of forming such compounds. Baeyer and Villiger (*Ber.*, 1902, **35**, 1210) have shown that it will combine with acids and phenols, and we have found that it combines equally readily with metallic salts and organo-magnesium halides. No regularity is observable in the proportion of cineol present in these; thus in its compounds with α- and β-naphthol and pyrogallol the constituents are present in molecular proportions, but one molecule of cadmium or zinc iodide, resorcinol, magnesium ethyl iodide, or of ferro- or ferri-cyanic acid combines with two molecules, whilst one molecule of cobalticyanic acid combines with three molecules of cineol. These compounds of cineol are in general decomposed by solvents or in a vacuum and have therefore little in common with the additive compounds of the phosphine oxides, some of which can be recrystallised from water (Part I, *loc. cit.*). This may be partly due to the volatility of cineol, but seems to indicate an influence of the phosphorus atom on the capacity of the oxygen atom in the oxides to form additive compounds. As is only to be expected from its similarity in constitution to cineol, cineolic acid also possesses the power of forming compounds with acids, although these are not formed with the same readiness. We find that diphenylsulphoxide, $(C_6H_5)_2SO$, combines with metallic salts and acids, whereas no such compounds of diphenylsulphone, $(C_6H_5)_2SO_2$, have been obtained, and its solubility in alcohol containing hydrochloric acid is the same as in absolute alcohol. In our investigation of the power of various substances containing oxygen to form these additive compounds, we have, after failure to obtain such by the ordinary methods, as a further test determined the solubility of the substance in (i) absolute alcohol, and (ii) the same solvent after passing in hydrogen chloride. In the cases where the solubility was the same we have assumed that the substance under examination does not form additive compounds. This assumption seems justifiable, since those substances which have yielded compounds with acids have not the same solubility in alcoholic hydrochloric acid as in alcohol, and, in general, substances which form additive compounds with acids also form them with metallic salts. Since diphenylsulphoxide * forms these compounds and the corresponding sulphone does not, it is probable that in the sulphone the oxygen and sulphur atoms are united in a ring in such a manner that any residual valencies of the same are mutually satisfied thus,  $R_2{:}S\langle{}^{O}_{O}$ or less likely  $R_2{:}S\langle{}^{O}_{O}$ (where the dots represent subsidiary valencies). This view is supported by the properties of such compounds as benzenesulpho-*p*-toluidide and benzenesulphonamide, which do not form these additive compounds. Were the formula for a sulphone  $R_2{:}S\lll^{O}_{O}$, it is not clear why there should be this difference in the behaviour of a sulphoxide $R_2{:}S{:}O$, if the slight basic properties of the latter are due to the oxygen atom. Similarly, the formulæ of nitrobenzene and

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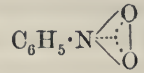
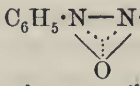
* An additive compound of dibenzylsulphoxide with hydrochloric acid has been recently described by Herrmann (*Ber.*, 1906, **39**, 3815).

azoxybenzene can be written $C_6H_5{\cdot}N{<}{O \atop O}$ and $C_6H_5{\cdot}\underset{\diagdown O \diagup}{N{-}N}{\cdot}C_6H_5$ and the non-formation of molecular compounds by these ascribed to the internal saturation of any residual or subsidiary valencies in the molecule.

We have been unable to prepare any additive product of a nitroso-compound with an acid, owing probably to the instability of this class of substances in the presence of acids, but have found that nitrosobenzene forms a stable compound with cadmium iodide of the formula $(C_6H_5{\cdot}NO)_5{\cdot}CdI_2$. It is therefore probable that the bimolecular variety of so many of these nitroso-compounds should be formulated, $R{\cdot}N{:}O\cdots O{:}N{\cdot}R$, rather than, $R{\cdot}N{<}{O \atop O}{>}N{\cdot}R$, as mere solution of the colourless bimolecular variety yields the unimolecular form.

It may be pointed out that the green or dark blue substances of the type of nitrosodimethylaniline (or *p*-nitrosoaniline), which is best formulated $\overline{O{\cdot}N{:}C_6H_4{:}N}Me_2$ (see O. Fischer and Hepp, *Ber.*, 1887, **29**, 1252), give with acids yellow compounds of the nature of salts, whilst the additive compounds with metallic salts are all blue or blue-green. It is probable that the former class of these substances are of the general type, $HO{\cdot}N{:}C_6H_4{:}NMe_2X$, in which the nitrosoamine behaves as a mono-acid base, whilst the latter owe their formation to the subsidiary valencies of the oxygen atom. The platinichloride of "*p*-nitrosodimethylaniline" must be excepted from this statement, and several other examples of additive compounds containing hydrogen platinichloride, which are anomalous in constitution have been obtained. Several of such have been summarised by Morgan and Micklethwait (Trans., 1906, **89**, 868), and, with other compounds described in our communications, cannot be formulated on the simple oxonium type.

These results naturally led to the question as to whether the salts and molecular compounds formed by amides are due to the further combining power of the nitrogen or of the oxygen atoms.

It has already been suggested by Werner (*Annalen*, 1902, **322**, 296) that the salts of carbamides owe their existence rather to the subsidiary valency of the oxygen atom of the $:C:O\cdots$ group than to that of the two nitrogen atoms, since, for example, a dinitrate of carbamide might be expected to exist, whereas only a mononitrate is known.

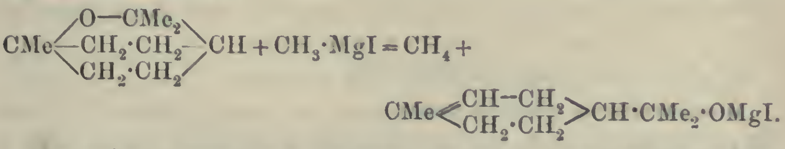
An examination of the literature shows that this is very probable, since the molecular proportion of carbamide in its additive compounds with acids (and metallic salts) is very variable and not compatible with the usually regular increase of the valency of one or both of the nitrogen atoms from three to five. Our investigation of the aryl-substituted carbamides affords some further evidence. Contrary to the statements in most text-books, mono-aryl carbamides do form compounds with acids, which exhibit much variation in stability, whilst di- and tetra-aryl carbamides are more soluble in alcoholic hydrochloric acid than in alcohol, form additive compounds with metallic salts, and in common with all carbamides form additive compounds with organo-magnesium halides, which are decomposed by water with the liberation of the carbamide.

Further, compounds of acetanilide with hydrochloric acid have long been known, whilst the solubility of benzanilide in alcoholic hydrochloric acid is greater than in alcohol. It has already been mentioned that the amides of aryl-sulphonic acids do not form additive compounds, and it is well known that a hydrogen atom of the NH_2 group in these is readily replaceable by an electropositive atom.

The formation of salts and additive compounds of carbamides may therefore be regarded as due to the residual or subsidiary valency of the oxygen atom. The relative stability of compounds, as, for example, carbamide hydrogen nitrate, or trimethylphosphine oxide hydrogen dichromate (Part I, *loc. cit.*), compared with that of the additive compounds of cineol, can be regarded as due to the influence of the nitrogen or phosphorus atom on the subsidiary valency of the oxygen atom.

Reaction of Cineol with Organo-magnesium Halides.

When cineol is added to an ethereal solution of an organo-magnesium halide, a yellowish-white precipitate is formed. If this is decomposed by dilute acids in the usual manner, cineol is almost quantitatively regenerated. If, however, the precipitate is heated for some time at about 170—190°, a saturated hydrocarbon is evolved, and the powder remaining, when decomposed with dilute acids, yields terpineol [Δ^1-*p*-menthenol(8)]. The reaction, which is a very violent one, can be represented as follows:



$$\mathrm{CMe}\left\langle\begin{matrix}\mathrm{O{-}CMe_2}\\ \mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CH} + \mathrm{CH_3{\cdot}MgI} = \mathrm{CH_4} +$$

$$\mathrm{CMe}\left\langle\begin{matrix}\mathrm{CH{-}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\right\rangle\mathrm{CH{\cdot}CMe_2{\cdot}OMgI}.$$

The action of cineol on a Grignard reagent is therefore the replacement of the ether with the formation of an oxygen additive compound of cineol with the alkyl magnesium halide. This additive compound, when heated, undergoes intramolecular change with the formation in the first place of derivatives of terpineol, which, if the heating is not kept under control, polymerise to hydrocarbons containing twenty or more carbon atoms. A similar series of reactions takes place if a mixture of cineol, ethyl iodide, benzene, and magnesium is warmed on a water-bath, whilst the same mixture, without the benzene, reacts with explosive violence when heated on a sand-bath, but under these conditions very little, if any, terpineol is formed, the main product being *p*-cymene. It is noteworthy, however, that with or without the benzene an additive compound is formed, and if the mixture is not allowed to get warm, this regenerates cineol on treatment with cold dilute acids. In no instance was the formation of any terpin hydrate observed.

Since most compounds of the character of anhydrides form additive compounds with magnesium alkyl halides, this type of reaction may prove of service with substances, which like cineol are not easily hydrolysed.

EXPERIMENTAL.

The additive compounds of cineol with the two naphthols, briefly described by Henning (D.R.-P. 1897, 100551), were analysed and each found to contain molecular proportions of the two constituents. The compound with α-naphthol melted at 78°, and when distilled in steam in the presence of sodium hydroxide left behind 47·7 per cent. of naphthol. (Theoretical for molecular proportions = 48·3 per cent.) The compound with β-naphthol melted sharply at 50°, and gave 47·9 per cent. of β-naphthol.

Cineol hydrogen cobalticyanide, described but not analysed by Baeyer and Villiger (*loc. cit.*), gave on titration $H_3Co(CN)_6 = 32{\cdot}7$, and was unaltered at the end of three days after remaining in a vacuum.

$(C_{10}H_{18}O)_3{\cdot}H_3Co(CN)_6$ requires $H_3Co(CN)_6 = 32{\cdot}3$ per cent.

Cineol zinc iodide * is slowly deposited in the form of small, colourless prisms from an alcoholic solution of zinc iodide containing cineol. These become pasty when heated at 75—80°, and melt at 130—131°, giving two layers. The compound, which is not deliquescent, is decomposed by hot water, and slowly loses its cineol when heated at 100—105°, leaving 50·6 per cent. of zinc iodide.

$(C_{10}H_{18}O)_2{\cdot}ZnI_2$ requires $ZnI_2 = 50{\cdot}7$ per cent.

Cineol cadmium iodide is very similar to the zinc iodide. It forms large, colourless cubes, has no definite melting point, and is stable in air at the ordinary temperature. Analysis gave $CdI_2 = 54{\cdot}3$.

$(C_{10}H_{18}O)_2{\cdot}CdI_2$ requires $CdI_2 = 54{\cdot}2$ per cent.

Cineolic acid forms a *compound* with hydrogen cobalticyanide, which separates in pale yellow crystals from alcohol, and does not melt below 285°. Analysis gave $N = 10{\cdot}2$.

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* As a rule, substances containing oxygen form additive compounds more readily with metallic salts, which are only slightly ionised.

$(C_{10}H_{16}O_5)_3{\cdot}H_3Co(CN)_6$ requires $N = 9{\cdot}7$ per cent.

Compounds with Diphenylsulphoxide.

Diphenylsulphoxide cadmium iodide crystallises from a concentrated alcoholic solution of the two components in hard, irregular nodules. It can be recrystallised from dilute alcohol and melts at 136°. Analysis gave $Cd = 14{\cdot}6$; $I = 33{\cdot}4$.

$\{(C_6H_5)_2SO\}_2{\cdot}CdI_2$ requires $Cd = 14{\cdot}5$; $I = 33{\cdot}1$ per cent.

Diphenylsulphoxide hydrogen platinichloride is obtained in a similar manner, and forms hard, irregular crystals, which melt at 128°. Analysis gave $Pt = 13{\cdot}5$; $H_2PtCl_6 = 28{\cdot}5$; $C = 50{\cdot}8$; $H = 4{\cdot}4$.

$\{(C_6H_5)_2SO\}_5{\cdot}H_2PtCl_6$ requires $Pt = 13{\cdot}6$; $H_2PtCl_6 = 28{\cdot}8$; $C = 50{\cdot}8$; $H = 3{\cdot}7$ per cent.

Diphenylsulphoxide hydrogen aurichloride separates from an alcoholic solution of the two components in orange-yellow prisms, which melt at 117—118°. Analysis of a specimen recrystallised from 96 per cent. alcohol gave $Au = 26{\cdot}5$.

$\{(C_6H_5)_2SO\}_2{\cdot}HAuCl_4$ requires $Au = 26{\cdot}4$ per cent.

Diphenylsulphoxide hydrogen ferrocyanide separates from an alcoholic solution of the two components in white or very pale green crystalline plates, which slowly turn blue on heating, and have no definite melting point. Analysis gave $H_4Fe(CN)_6 = 34{\cdot}5$.

$\{(C_6H_5)_2SO\}_2{\cdot}H_4Fe(CN)_6$ requires $H_4Fe(CN)_6 = 34{\cdot}8$ per cent.

Compound of Nitrosobenzene with Cadmium Iodide.

The green alcoholic solution of nitrosobenzene, when mixed with an alcoholic solution of cadmium iodide, slowly deposits very small, white crystals. These melt at 114°, are slowly decomposed by cold, more quickly by hot, water, and give a green solution in alcohol, from which the compound can be repeatedly recrystallised without alteration. A product, which had been recrystallised five times from alcohol without undergoing change, on analysis gave $Cd = 15{\cdot}0$; $CdI_2 = 49{\cdot}4$.

$(C_6H_5{\cdot}NO)_5{\cdot}CdI_2$ requires $Cd = 15{\cdot}1$; $CdI_2 = 49{\cdot}4$ per cent.

Compounds of p-*Nitrosodimethylaniline.*

The compounds of nitrosodimethylaniline with acids which are described in the literature (see Beilstein, 3te Auf. II. 329) are all yellow or yellowish-red. We have in addition prepared the following salts, which are all yellow, crystalline substances; the *trichloroacetate*, $HO\cdot N\colon C_6H_4\colon NMe_2\cdot CO\cdot CCl_3$, which melts at 103°; the *picrate*,

$$HO\cdot N\colon C_6H_4\colon NMe_2\cdot O\cdot C_6H_3(NO_2)_3,$$

which decomposes at 140°; the *cobalticyanide*,*

$$\{ON\cdot C_6H_4\cdot NMe_2\}_3\cdot H_3Co(CN)_6,$$

which decomposes at about 185°, and the *platinichloride*,*

$$\{ON\cdot C_6H_4\cdot NMe_2\}_3\cdot H_2PtCl_6,$$

which decomposes violently at 183° and is anomalous in constitution.

p-*Nitrosodimethylaniline zinc chloride*, which is to be regarded as an oxygen additive compound, crystallises from an alcoholic solution of the components in steel-blue plates with a metallic lustre. These yield a carmine-red powder, which melts and decomposes at 176°. Analysis gave N = 13·2.

$\{N(CH_3)_2\colon C_6H_4\colon NO\}_2\cdot ZnCl_2$ requires N = 12·9 per cent.

Additive Compounds of Carbamides.

Carbamide hydrogen platinichloride (compare Heintz, *Annalen*, 1879, **198**, 91), obtained from an alcoholic solution of the components, crystallises from dilute hydrochloric acid in red, prismatic rhombs and melts at 119—120°. Analysis gave Pt = 30·0.

$\{CO(NH_2)_2\}_4\cdot H_2PtCl_6$ requires Pt = 29·8 per cent.

Phenylcarbamide hydrogen chloride crystallises from a solution of the carbamide in alcoholic hydrochloric acid in white, pearly leaflets. It melts and evolves gas at 114—116°, is fairly stable in dry air, but slowly evolves hydrogen chloride in moist air, being readily decomposed by water. Analysis of different specimens gave HCl = 20·8 and 21·0.

$C_6H_5\cdot NH\cdot CO\cdot NH_2\cdot HCl$ requires HCl = 21·2 per cent.

Phenylcarbamide hydrogen nitrate is obtained when a solution of the carbamide in warm concentrated nitric acid is allowed to cool. It separates in colourless leaflets, which melt and decompose at 134—135°. It is fairly stable in dry air and is decomposed by water, yielding the carbamide. Titration gave HNO_3 = 31·5.

$C_6H_5\cdot NH\cdot CO\cdot NH_2\cdot HNO_3$ requires HNO_3 = 31·7 per cent.

Phenylcarbamide hydrogen aurichloride separates from an alcoholic solution of the components containing hydrochloric acid, in chocolate-red, prismatic needles, which melt at 147° and are decomposed by water. Analysis gave Au = 32·1.

$\{C_6H_5\cdot NH\cdot CO\cdot NH_2\}_2\cdot HAuCl_4$ requires Au = 32·1 per cent.

Phenylcarbamide hydrogen platinichloride is obtained in an analogous manner to the aurichloride, and forms pale orange-coloured crystals, which begin to darken at about 165° and decompose at 173—175°. Analysis gave Pt = 23·0.

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* To save space, these are not printed in the quinonoid form.

$\{C_6H_5\cdot NH\cdot CO\cdot NH_2\}_3\cdot H_2PtCl_6$ requires Pt = 23·7 per cent.

o-Tolylcarbamide hydrogen trichloroacetate.—o-Tolylcarbamide dissolves in fused trichloroacetic acid and, on cooling, the additive compound crystallises out. The product, after draining on a porous tile, has usually a green tinge, is decomposed by solvents, and melts at 94—98°. Titration gave $CCl_3\cdot CO_2H = 52\cdot 5$.

$CH_3\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2\cdot CCl_3\cdot CO_2H$ requires $CCl_3\cdot CO_2H = 52\cdot 2$ per cent.

β-Naphthylcarbamide hydrogen chloride crystallises from alcohol containing hydrochloric acid in very lustrous, white leaflets, which melt and decompose at 154°, are decomposed by moisture, but are fairly stable in dry air. Analysis gave HCl = 15·9.

$C_{10}H_7\cdot NH\cdot CO\cdot NH_2\cdot HCl$ requires HCl = 15·7 per cent.

Tetraphenylcarbamide ferric chloride separates from anhydrous alcoholic solutions of the components in large, hexagonal tablets (often 3 mm. across) which melt at 54—55°. Analysis gave Fe = 6·3.

$\{[(C_6H_5)_2N]_2CO\}_2\cdot FeCl_3$ requires Fe = 6·3 per cent.

Carbamides in general and substituted oxamides are only slightly soluble in anhydrous ether. These dilute solutions, however, when mixed with a Grignard reagent, form white precipitates which are difficult to analyse on account of their hygroscopic nature. When treated with dilute acids they yield the original amide, and can therefore be regarded as compounds analogous to Grignard reagents in which the ether is replaced by the amide, the formation of each being due to the subsidiary valencies of the oxygen atom in the ether or amide respectively.

Relative Solubility of Various Substances in Absolute Ethyl Alcohol and in a Solution of Hydrogen Chloride in Absolute Ethyl Alcohol.

Saturated solutions of the substances were made at about 35° in the two solvents, and these were allowed to attain the temperature of the room, when 5 c.c. of the clear supernatant solution were drawn off into tared flasks and the solvents evaporated. In each case the melting point of the recovered substance was determined to prove that no alteration had taken place. The following dissolve to approximately the same extent in both solvents: diphenylsulphone, benzenesulphonamide, benzenesulpho-*p*-toluidide, *m*-dinitrobenzene, and azoxybenzene. The following are more soluble in alcoholic hydrochloric acid: diphenylsulphoxide, benzanilide (about four times), diphenylcarbamide (about seven times), tetraphenylcarbamide (about three times), oxanilide (about three times).

Cineol and Alkyl Magnesium Halides.

On the addition of a dry ethereal solution of cineol to one of magnesium ethyl iodide a yellowish-white precipitate separates. On analysis this gave Mg = 5·2.

$(C_{10}H_{18}O)_2\cdot EtMgI$ requires Mg = 4·9 per cent.

The compound is very hygroscopic, decomposing with the formation of cineol. If the conditions are reversed, the Grignard reagent in excess being poured into the solution of cineol, no precipitate is formed, and after distilling off the ether a viscous oil remains. When this oil is heated in the oil-bath at 170—190° for some hours, it slowly changes into a hard, dry mass, and at the same time evolves an inflammable and saturated gas (ethane), which is not condensed at the temperature of a mixture of ice and salt. It is necessary that the temperature should be allowed to rise very slowly, as otherwise below 190° the explosive reaction, which usually sets in at about 195° may be started, when much iodine is liberated and a little *p*-cymene with a quantity of highly polymerised products is obtained. The powdered mass reacts vigorously with dilute sulphuric acid cooled to below 0°, and leaves a pale yellow oil which can be separated into two portions by distillation with steam. The volatile portion after extraction with ether can be fractionated under reduced pressure, and yields terpineol with traces of unchanged cineol. A similar result is obtained, if the additive compound described above is heated alone, except that much cineol remains unchanged. The identity of the product with Δ^1-*p*-menthenol-(8) was proved by its boiling point, 107°/18 mm. and melting point, 35°, and by the preparation and analysis of the following derivatives: the phenylcarbamide (m. p. 110°), the nitrosochloride (m. p. 120°), the nitrolanilide (m. p. 151°), the nitrolpiperidide (m. p. 160°), and terpin hydrate. The heating of the oil in this way is conveniently carried out in 60 gram lots in Winchester quart bottles immersed in oil-baths. The operation requires careful watching, as the material froths when the excess of the Grignard reagent decomposes at about 140°. The best yields were obtained when 2½ molecular proportions of magnesium ethyl iodide and 1 of cineol were employed. Three operations (60 grams each), carried out simultaneously, gave 75 grams of pure terpineol, which when cooled and seeded solidified completely.

Magnesium methyl iodide or magnesium ethyl bromide can be used with equally good results. Small quantities of dipentene are also formed, but in successful operations the amount is less than 1 per cent. That portion of the products not volatile with steam was fractionated. The lower fraction, b. p. 191°/18 mm., was an oil, which gave on analysis $C = 88{\cdot}3$; $H = 12{\cdot}2$, and molecular weight by cryoscopic method $= 272$.

$C_{20}H_{32}$ requires $C = 88{\cdot}3$; $H = 11{\cdot}8$ per cent., and M.W. $= 272$.

The oil is therefore a diterpene. The higher fraction, b. p. about 240°/18 mm., was deep yellow, and was not further investigated.

MUNICIPAL TECHNICAL SCHOOL,
BLACKBURN.

LXXXIV.—*Freezing Point Curves of the Menthyl Mandelates.*

By ALEXANDER FINDLAY and EVELYN MARION HICKMANS.

ON determining the freezing points of mixtures of two substances miscible with each other in the liquid, but not in the solid state, two types of curves are obtained, according as the two components yield or do not yield a compound or compounds which are stable in contact with the fused mass. In the latter case the freezing point curve will consist of two branches meeting in an eutectic point; in the former case, there will be one or more intermediate curves, according to the number of stable compounds formed.

The same method of investigation can be applied in the case of optically active substances in order to decide whether a resolvable inactive body is a mixture of the two oppositely active constituents (a *dl*-mixture), or a racemic compound (H. W. B. Roozeboom, *Zeitsch. physikal. Chem.*, 1899, **28**, 494). In the case of such substances, the freezing point curve must be symmetrical about a line representing a mixture of 50 per cent. of either of the constituents, but this symmetry will again disappear in the case of partially racemic substances, for in such cases the melting points of the constituents are no longer the same. As no freezing point curves of partially racemic substances had been determined, we have sought to fill up the gap by a study of the freezing point curves of the *l*-menthyl esters of *d*- and *l*-mandelic acid.

It has already been shown by J. H. Adriani (*Zeitsch. physikal. Chem.*, 1900, **33**, 453) that inactive mandelic acid exists, at the temperature of its melting point, as a racemic compound, and, under the same conditions, we have found that the *l*-menthyl ester of *r*-mandelic acid also occurs as a definite compound. This is evident from the existence of the intermediate curve (Fig. 2), the flattened summit of which indicates, however, a certain amount of dissociation in the liquid phase. That *l*-menthyl *r*-mandelate is stable also at the ordinary temperature has been indicated by A. McKenzie (Trans., 1904, **85**, 1255), and solubility measurements, on which we are at present engaged, prove this to be so. Indeed, it is probable that the transition temperature at which *l*-menthyl *r*-mandelate breaks up into a conglomerate of *l*-menthyl *d*-mandelate and *l*-menthyl *l*-mandelate lies below, probably considerably below, 0°. We hope soon to obtain more exact information on this point.

It has been said above that the flattened summit of the freezing point curve indicates a certain amount of dissociation of the partially racemic compound in the liquid state, and it appeared of interest to attempt to calculate, if only approximately, the degree of dissociation. This is all the more of interest on account of the fact that the existence of a racemic compound in the liquid state has been considered to be very doubtful, if it has not been altogether denied. Ladenburg (*Ber.*, 1895, **28**, 163, 1991) has asserted the existence of racemic coniine, but his evidence has not been accepted as convincing, and in the case of other inactive liquids, such as inactive tetrahydroquinaldine and inactive pinene, W. J. Pope and S. J. Peachey (Trans., 1899, **75**, 1111) concluded that the optically active antipodes when mixed do not form a racemic compound. It may, however, be doubted whether the methods employed were altogether capable of deciding the question, for one must expect, on the basis of the laws of equilibrium, the formation to a greater or smaller extent, perhaps, indeed, only to an inappreciable extent, of the racemic compound.

Although, in the case of substances known only in the liquid state, no general method has as yet been obtained to establish in a sufficiently convincing manner the existence of liquid racemates; still evidence is not wanting that racemates do exist, not only in the liquid state, but also in solution. Thus, A. Byk (*Zeitsch. physikal. Chem.*, 1904, **49**, 682) has shown that the colour of a solution of alkali copper tartrate (prepared from active tartaric acid) is different from that of an equally concentrated solution of alkali copper racemate, from which the existence of the latter in solution may be concluded. Evidence of the existence of racemic compounds in solution has also been obtained by G. Bruni and M. Padoa (*Atti R. Accad. Lincei*, 1902, [v], **11**, 212). More recently Brühl (this vol., 115) has shown that the liquid *dl*-$\Delta^{3:8(9)}$-*p*-menthadiene is probably a racemic compound.

Evidence of the existence of racemates in the liquid state is given by the freezing point curves of optically active substances obtainable in the crystalline form. It has already been remarked that when two components combine to form a compound stable at its melting point, the freezing point curve for mixtures of the two components will exhibit an intermediate portion which gives the conditions under which the compound can exist in contact with molten mixtures. Not only so, but it is possible, from the shape of this curve, to gain some idea of the stability of the compound or of the degree to which the compound undergoes dissociation in the liquid state. The curvature of the summit of the curve is greater the more the compound is dissociated into its components in the liquid state. The smaller the degree of dissociation, the sharper will be the summit of the curve, and if the compound is completely undissociated in the liquid state the two branches of the curve will intersect. This is found, for example, in the case of pyridine and methyl iodide (A. H. W. Aten, *Zeitsch. physikal. Chem.*, 1905, **54**, 124).

Since the flattening of the freezing point curve of the compound is due to the lowering of the freezing point produced by the presence of the products of dissociation, it is possible to calculate the degree of dissociation with the help of the law of mass action and from a knowledge of the depression produced by the addition of a known amount of one of the components. This method has been applied by R. Kremann (*Monatsh.*, 1904, **25**, 1215; *Zeitsch. Elektrochem.*, 1906, **12**, 259) and a graphic method by H. W. B. Roozeboom and A. H. W. Aten (*Zeitsch. physikal. Chem.*, 1905, **53**, 463).

Although it must be admitted that the assumption underlying the method may not be completely fulfilled, and although the method can, at best, be considered as giving only approximately correct results, we have nevertheless thought it worth while to make use of it as giving some idea of the degree of dissociation of the partially racemic menthyl *r*-mandelate.

The law of mass action applied to the dissociation of the binary compound into its two components yields the expression

$$\frac{x}{100+x}\cdot\frac{x}{100+x}=k.\frac{100-x}{100+x},$$

where x is the percentage number of molecules of each of the components produced by the dissociation, and $100+x$ is the total number of molecules. From this we can calculate the value of k for any given value of x, that is, for any given degree of dissociation. If, now, an excess of a gram-molecules of one of the components is added, the dissociation will be altered in approximate accordance with the expression:

$$\frac{x+a}{100+x+a}\cdot\frac{x}{100+x+a}=k.\frac{100-x}{100+x+a},$$

from which the new value of x can be calculated. We are thus enabled to calculate the actual number of molecules which have a depressing effect on the freezing point. If we also know the value of the molecular depression of the freezing point, we can calculate the course of the freezing point curve for mixtures of different composition and for any assumed value of dissociation. It only remains therefore to compare the actual freezing point curve with those calculated in the above manner for different degrees of dissociation.

The value of the depression of the freezing point produced by one gram-molecule of solute in 100 gram-molecules of solvent can be obtained by means of the van't Hoff formula, $\delta = \frac{0{\cdot}02\ T^2}{M.\ L.}$, where L is the latent heat of fusion. We preferred, however, to obtain it by determining the lowering produced by a known amount of mandelic acid. It must be conceded that this method is not altogether free from objection since Kremann (*loc. cit.*) has shown that, in the case of several organic compounds, the values so obtained are not altogether in harmony. An error may therefore enter into the calculation from this source, but we do not consider it to be a large one, and, moreover, it must be recalled that we are dealing with only an approximate determination of the dissociation.

The value obtained for δ is 0·283°. Using this number, one obtains the following values for the depression of the freezing point of the partially racemic compound, assuming the degree of dissociation to be 35 and 50 per cent. respectively:

Degree of dissociation = 35 per cent.		Degree of dissociation = 50 per cent.	
Molar percentage of compound.	Depression of freezing point.	Molar percentage of compound.	Depression of freezing point.
100·0	—	100·0	—
94·4	0·03°	94·4	—
89·3	0·11	89·3	0·048°
83·3	0·41	83·3	0·11
74·1	0·71	74·1	0·29
66·6	1·26	66·6	0·49

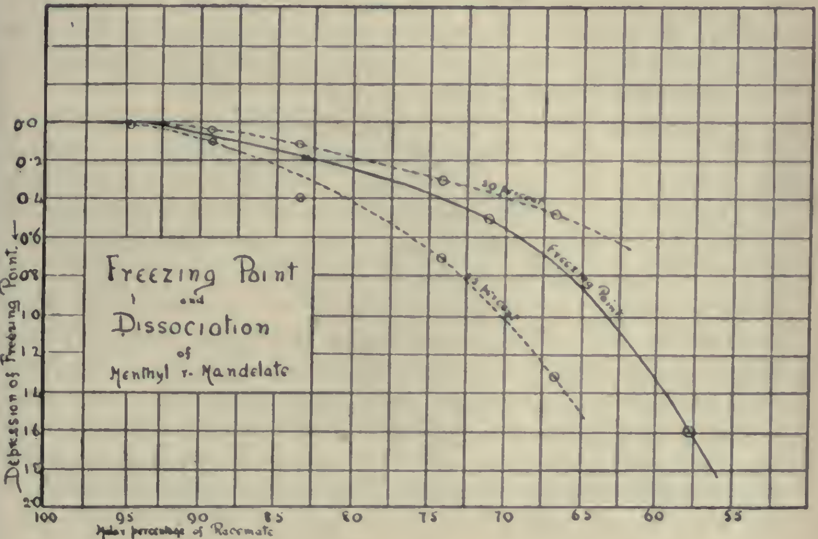
On the other hand, we obtain the following table from the experimentally determined freezing point curve:

Molar percentage of compound.	Freezing point.	Depression.
100·0	83·7°	—
83·3	83·5	0·2°
71·6	83·2	0·5
57·8	82·1	1·6

On plotting the above numbers in the same system of co-ordinates, the curves shown in Fig. 1 result. From this figure we see that the experimental freezing point curve lies between the curves calculated on the assumption that the degree of dissociation is 35 and 50 per cent. respectively. Although no great accuracy is claimed for the calculation, we are entitled to conclude from this that the *l*-menthyl *r*-mandelate exists in the liquid state at the temperature of its melting point, and that it is dissociated into its components to an extent of about 50 per cent.

On examining the freezing point curves obtained by Adriani (*loc. cit*) several cases are also found where the shape of the curve indicates the existence to a considerable extent of undissociated racemate in the liquid state. More especially is this the case with racemic benzoyltetrahydroquinaldine, the sharp curve for which indicates a comparatively small degree of dissociation.

FIG. 1.



EXPERIMENTAL.

l-*Menthyl* r-*mandelate* was prepared in the manner described by A. McKenzie (Trans., 1904, **85**, 383). It was crystallised from light petroleum and melted at 85—86°. Its specific rotation determined in ethyl-alcoholic solution was $[\alpha]_D^{11\cdot3}$ $-75\cdot03°$.

l-*Mandelic acid* was prepared from amygdalin and was converted into its *l*-menthyl ester by the hydrogen chloride method. The product was extracted with ether and the ethereal solution washed with dilute sodium carbonate solution. The ether was then evaporated, the residue poured into water, and subjected to steam distillation to remove the excess of menthol. The liquid was again extracted with ether, and, after evaporating off the latter, the residue was crystallised from alcohol. The product melted at 81° and had a specific rotation in alcoholic solution of $[\alpha]_D^{20}$ $-140\cdot92°$. The above method of treatment was adopted instead of distillation under reduced pressure (McKenzie, Trans., 1904, **85**, 1254) on account of the fact that in one preparation we obtained a partially racemised product.

d-*Mandelic acid* was obtained from the racemic acid by means of its cinchonine salt, and was converted into its *l*-menthyl ester in the same manner as *l*-mandelic acid. The ester, after crystallisation from alcohol, melted at 98° and gave a specific rotation in alcoholic solution of $[\alpha]_D^{17\cdot5}$ $-9\cdot45°$.

It may be noticed that the specific rotations obtained for the three esters are somewhat higher than those quoted by McKenzie (*loc. cit.*); they agree, however, very closely among themselves, the difference between the values of $[\alpha]_D$ for *l*-menthyl *l*-mandelate and *l*-menthyl *r*-mandelate being 65·89°, and that between *l*-menthyl *r*-mandelate and *l*-menthyl *d*-mandelate, 65·58°.

Determination of the Freezing Points.—The determinations of the freezing point were carried out in a moderately large test-tube surrounded by another tube to act as an air mantle, and the whole was immersed in a bath of glycerol. Both the inner tube and the bath were provided with a stirrer and thermometer, the bulb of the thermometer in the inner tube being immersed completely in the fused mixture the freezing point of which was being determined. On account of the great sluggishness with which crystallisation took place, extensive superfusion readily occurred, leading to too low values of the freezing point. We therefore adopted the plan of alternately lowering and raising the temperature of the bath very slowly in the neighbourhood of the freezing point, and so of approaching very nearly to the true freezing point. The difficulties were not so great in the case of mixtures from which the ester of the lævo-acid separated out, as this crystallised more rapidly than the other two esters. Special experiments showed that no marked racemisation occurred while the determination of the freezing point was being carried out.

The following is a table of the freezing points obtained, the numbers being also plotted in fig. 2.

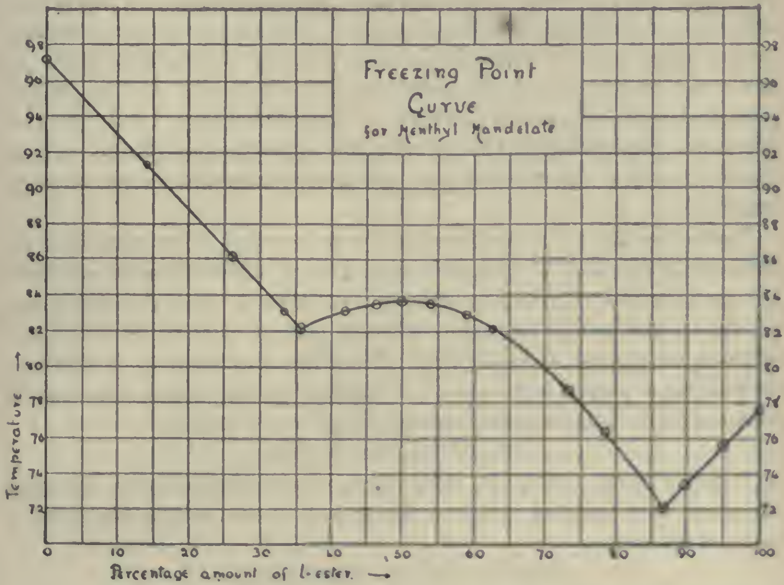
Lævo-ester, per cent.	Freezing point.	Lævo-ester, per cent.	Freezing point.
100·00	77·6°	54·65	83·5
94·88	76·0	50·00	83·7
89·03	73·8	45·87	83·7
86·57 *	72·4	41·77	83·6
85·17	72·8	36·15 *	82·3
77·63	76·2	33·63	82·7
72·92	78·5	26·08	86·1
63·54	82·1	14·03	91·5
58·26	88·2	0	97·2

* Eutectic mixture.

Molecular Depression of the Freezing Point.—In order to obtain the value of the freezing point constant, determinations were made of the freezing point of *l*-menthyl *r*-mandelate to which known weights of mandelic acid were added. The value of the constant *k* could then be calculated from the ordinary formula for the lowering of the freezing point.

0·0857 Gram of mandelic acid added to 3·871 grams of ester depressed the freezing point by 1·2°. Hence $k = 8240$.

FIG. 2.



Further addition of 0·0584 gram of mandelic acid caused a total depression of 2·0°. Hence $k = 8170$. Mean value of $k = 8205$.

From this we obtain, since the molecular weight of mandelic acid is 290, $\delta = \frac{k}{100M} = 0{\cdot}283$.

Part of the expense of the foregoing investigation was defrayed by a grant awarded by the Committee of the Research Fund, for which we wish to express our thanks.

CHEMICAL DEPARTMENT,
UNIVERSITY OF BIRMINGHAM.

LXXXV.—*Acyl-ψ-derivatives of Iminothiocarbamic Acid and their Isomerides.*

By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

IN the course of an investigation commenced a few years ago by one of us (Dixon, Trans., 1903, **83**, 550), it was observed that methyl chlorocarbonate unites spontaneously with phenylthiourea to form an additive compound, $C_7H_8N_2S,C_2H_3O_2Cl$. When heated, this substance readily loses carbon dioxide, thereby yielding the hydrochloride of Bertram's methyl ester of iminophenylthiocarbamic acid or iminophenylcarbaminethiomethyl, PhNH·C(NH)·SMe (*Ber.*, 1892, **25**, 49), otherwise methyl-ψ-phenylthiourea; the latter hydrochloride is produced directly if the constituents are heated together in presence of benzene.

From the facts (i) that Bertram's thiomethyl base can thus be obtained, whereas it is not derivable from a thiocarbamide in which the carboxymethyl group is already united to a nitrogen atom, and (ii) that a molecule of hydrogen chloride may be withdrawn from the additive compound, $C_7H_8N_2S,C_2H_3OCl$, with formation of a thiourea containing a phenyl and a carboxymethyl group, which thiourea is isomeric with the *ab*-carboxymethylphenylthiocarbamide,

$$PhNH{\cdot}CS{\cdot}NH{\cdot}CO_2Me,$$

of Doran (Trans., 1901, **79**, 908) there was no difficulty in drawing the conclusion that the additive compound is the hydrochloride of a basic or ψ-form,

$$PhNH{\cdot}C(NH){\cdot}S{\cdot}CO_2Me,HCl.$$

On the other hand, considerable difficulty was experienced in deciding by direct means the constitution of the substance left on removal of the halogen acid, but ultimately, on the ground that the hydrochloride could possess no other structure than that assigned in the preceding formula, it was conjectured that this residue must be the corresponding base, PhNH·C(NH)·S·CO_2Me. In other words, the constitution formulated for the base rested solely on the assumption that it was liberated unchanged and remained so. But more recent investigation of similar compounds, derived from monosubstituted thioureas and fatty acylogens, having shown that an acyl group, united initially to sulphur, is prone to move very readily to one of the nitrogen atoms as soon as the combined halogen acid is withdrawn, it became necessary to revise the facts in order to learn whether this assumption is warrantable.

That it is not, seems evident from the following considerations.

(i.) The hydrochloride melts at 87°; the "base" liberated from this by treatment with alkali in the cold is, as might be expected, an oil. It does not, however, long remain liquid, but, even during the process of precipitation if this is conducted by the slow addition of the alkali, changes to a solid, the melting point of which, 166—167°, is remarkably high compared with that of the parent hydrochloride.

(ii.) Whilst the pure hydrochloride is freely soluble in water, the "base," on the other hand, when it has solidified, is practically insoluble in dilute or concentrated hydrochloric acid.

(iii.) The hydrochloride gives, in aqueous or weak alcoholic solution, a nearly insoluble picrate, whereas the "base" does not appear capable of yielding a picrate.

(iv.) The "base" is but slightly desulphurised by boiling with moderately strong alkali and a lead salt, whereas it might be anticipated that a combination such as $PhNH{\cdot}C(NH){\cdot}S{\cdot}CO_2Me$, except in so far as it might yield mercaptan (on account of the heating), would undergo quantitative desulphurisation. By the treatment named, the hydrochloride is easily and copiously desulphurised, whilst a little mercaptan escapes; thiocyanate is formed also, to a certain extent.

(v.) The solidified "base," if boiled with caustic alkali, yields no mercaptan; the resultant solution which contains, (iv), but little sulphide, gives an abundant reaction for thiocyanic acid.

The conclusion which we draw from these facts is, that the compound liberated from the hydrochloride, at least when the former has solidified, is not the corresponding base, but an isomeride. Since, as stated already, it is isomeric with *ab*-carboxymethylphenylthiocarbamide, $PhNH{\cdot}CS{\cdot}NH{\cdot}CO_2Me$, the only constitution which remains for it (neglecting mere tautomeric variants) is the *aa*-form, $PhN(CO_2Me){\cdot}C(NH){\cdot}SH$. Similar considerations apply, of course, in respect of the homologues described in the paper named.

Hugershoff, who was the first to obtain acyl unsymmetrical derivatives of this type,* including simple fatty radicles only, made the curious discovery that they are decomposed by contact with strong alkali into thiocyanic acid and substituted amide, whereas in weak alkali they dissolve without decomposition, but with internal molecular change into the isomeric form of *ab*-disubstituted thiocarbamide (*Ber.*, 1899, **32**, 3649).

Quite recently it has been shown (Dixon and Hawthorne, this vol., 122) that acetyl chloride unites spontaneously with phenylthiourea to form a hydrochloride, from which, by cautious elimination of the combined halogen acid, there is obtained, not the corresponding base, PhNH·C(NH)·SAc, but, instead, Hugershoff's *aa*-acetylphenylthiocarbamide, $AcPhN\cdot CS\cdot NH_2$, or, it may be, the thiourea,*

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* He supposed his acetylphenyl derivative to be an *ab*-compound and, consequently, the known acetylphenylthiocarbamide to have the *aa*-configuration Wheeler showed, however (*Amer. Chem. J.*, 1902, **27**, 274), that the converse view must be adopted.

AcPhN·C(NH)·SH.

By analogy, this tends to confirm the view originally entertained (Dixon, *loc. cit.*, 561) with regard to the chlorocarbonate "base" (but ultimately abandoned on the ground previously stated), that in it both radicles are joined to a single nitrogen atom.

In point of stability there are marked differences between the *aa*-disubstituted acetyl and the carboxymethyl derivatives. Thus, whilst the former are destroyed instantly by contact with cold strong alkali, the latter are attacked by it with some difficulty, although they yield thiocyanic acid at once when the mixture is heated. The former dissolve readily in cold dilute alkali with isomeric change to the *ab*-form; the latter do not dissolve and are unaffected. The former, when melted, undergo the same isomeric change as is induced by dissolution in weak alkali; the latter melt with decomposition and effervescence.

Further experiments have now been conducted on the interaction of various acid chlorides and thioureas, an account of which we have the honour to place before the Society.

Ethyl Chlorocarbonate and Phenylthiourea.

To finely-divided phenylthiourea, made into a thin paste with tepid alcohol, the chlorocarbonate was slowly added, the mixture becoming clear when about 1 molecular proportion had been used; thus, 6·1 grams of the former required 4·46 grams of the latter, instead of 4·35 calculated from the equation:

$$PhNH\cdot C(NH)\cdot SH + EtO\cdot COCl = PhNH\cdot C(NH)\cdot S\cdot CO_2Et,HCl.$$

The product, a yellow acid syrup, showing no tendency to crystallise on keeping, was soluble in cold water to an opalescent solution; this yielded with picric acid an orange-yellow picrate, and was freely desulphurised by warming with an alkaline solution of lead.

On careful neutralisation of the dilute aqueous solution of the hydrochloride by weak caustic alkali, droplets of oil were precipitated, changing by degrees to a granular solid; the latter, when crystallised from boiling alcohol, in which it is moderately soluble, although but sparingly so in the cold, formed brilliant, white, flattened prisms, free from chlorine, and melting without immediate effervescence at 132—133°.

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* The name "thiourea" is used to denote $NH_2\cdot C(SH){:}NH$ or its substitution products; derivatives of $CS(NH_2)_2$ are termed "thiocarbamides" (see Trans., 1895, 67, 564).

Analysis gave the figures for a carboxyethylphenylthiocarbamide, $CSN_2H_2Ph{\cdot}CO_2Et$.

0·224, fused with $NaOH + KNO_3$, required 20·1 c.c. $N/10$ $BaCl_2$. S = 14·35.

0·448, by Kjeldahl's method, required 40·5 c.c. $N/10$ H_2SO_4. N = 12·65.

$C_{10}H_{12}O_2N_2S$ requires S = 14·29 ; N = 12·50 per cent.

There is no very considerable difference between the characters just mentioned and those recorded by Doran (Trans., 1896, **69**, 326) for *ab*-carboxyethylphenylthiocarbamide, namely, monoclinic tables melting at 130°. Nevertheless, the substances are distinctly isomeric, for whilst the *ab*-compound dissolves in warm dilute potash, but even after boiling with this reagent is precipitated unchanged by hydrochloric acid (*loc. cit.*), our compound, when gently warmed with alkali, decomposed, yielding a turbid mixture; this, when acidified and treated with ferric chloride, gave an intense blood-red coloration, thereby showing the presence of much thiocyanic acid. To make certain, we have re-examined the *ab*-derivative and find that under this treatment it yields no trace of thiocyanic acid.

As regards stability in contact with water, the hydrochloride is more resistant than the analogous derivative containing acetyl, namely, $PhNH{\cdot}C(NH){\cdot}SAc,HCl$, since on dissolution in water this is hydrolysed rapidly into hydrochloric and acetic acids with precipitation of phenylthiourea. Water, nevertheless, acts on the salt, for, on allowing the dilute aqueous solution to stand for some days, it gradually became turbid and needles were deposited. A like change occurred forthwith on heating the aqueous solution to about 50°, the product, after recrystallisation from alcohol, melting in each case at 132—133°, and hence not consisting of phenylthiourea. It had all the properties of the material precipitated by alkali, and when equal parts of the two were mixed together, the melting point underwent no change.

Water, therefore, like caustic alkali, eliminated only the combined hydrogen chloride from the additive compound. But the relatively high melting point of the solidified product, and especially the facts that the solid neither dissolved in hydrochloric acid nor gave a picrate, and moreover that the hydrochloride, when heated with alkali, yielded mercaptan, whereas the above solid did not—all these, viewed in connexion with the isomerism previously mentioned, serve to indicate that the substance melting at 132—133° is *aa*-carboxyethylphenyl-thiourea, $PhN(CO_2Et)·C(NH)·SH$, or its thiocarbamidic tautomeride, $PhN(CO_2Et)·CS·NH_2$.*

This evidence, although cumulative, is indirect; it still remained to be shown that the two groups, phenyl and carboxyethyl, are really joined to one and the same nitrogen atom. That such is the case may be concluded from the results of the following experiments.

A quantity of the pure compound (m. p. 132—133°) was covered with strong (15 : 100) aqueous caustic soda (3 mols.). No sign of action was noticeable at first, but presently the liquid grew slightly turbid, the outline of the crystals becoming somewhat indistinct; after two hours' standing, the mixture was gently warmed, whereupon the solid fused, thus showing that chemical action had taken place; the mixture was now extracted with ether, which dissolved the solid, the ethereal extract allowed to evaporate, and the aqueous portion diluted with water.

On evaporation of the ether, a dry solid was left containing no aniline; it retained, however, even after several recrystallisations from light petroleum, a trace of some desulphurisable impurity, and melted at about 48°. When heated in a dry tube, it gave the odour of phenyl *iso*cyanate, and hence consisted substantially of phenylurethane, $PhNH·CO_2Et$, melting, according to Wilm and Wischin (*Annalen*, 1868, **147**, 157), at 51·5—52°.

As no mercaptan had been evolved during the attack by caustic alkali, the whole of the sulphur initially present (save the mere trace in the ethereal extract) must have been in the aqueous portion. This, when mixed with a lead salt, remained perfectly clear, showing the absence of sulphide; when the mixture was boiled, it became only faintly brown, and hence contained practically none of the original sulphur compound; much thiocyanic acid, of course, was present, but neither carbonate nor aniline could be detected. Presumably, therefore, the action had proceeded according to the equation:

$$PhN(CO_2Et)·CS·NH_2 + NaOH = PhNH·CO_2Et + NaSCN + H_2O.$$

A quantitative experiment, conducted on the lines just indicated, gave the following results.

2·24 Grams, decomposed with alkali, gave 1·69 grams of (crude) phenylurethane, the calculated figure being 1·65 grams. The alkaline liquor from this was made up to 100 c.c., and the thiocyanic acid determined by Barnes and Liddles' method, using *N*/10 copper sulphate. Twenty c.c. required 19·4 c.c. of the solution, corresponding to 0·572 gram HSCN in the whole 100 c.c., whilst the amount, according to the equation given above, would be 0·59 gram.

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* As there is, at present, no means of deciding between these two structural formulæ for *aa*-compounds, the latter alone will be used in what follows; merely in order to avoid repetition, but not with the intention to advance one as preferable to the other.

Therefore, in the circumstances given, the decomposition of the *aa*-compound by strong caustic alkali into thiocyanic acid and phenylurethane is very nearly quantitative.

Hugershoff, in the paper already cited, mentions as a distinction between labile (that is, *aa*-) and stable (or *ab*-) acetylphenylthiocarbamide that the former is desulphurised in alcoholic solution by mercuric oxide, whilst the latter is not affected. Experiments now made with the corresponding *aa*- and *ab*-carboxyethylphenylthiocarbamides show that in this class the distinction does not hold good. Both compounds, when brought into contact with precipitated mercuric oxide, were desulphurised, the only difference noticed being that the change occurred much more slowly in the case of the *ab*-derivative.

Whilst the acyl group of a fatty acid in *aa*-disubstitution derivatives, such as $PhAcN\cdot CS\cdot NH_2$, moves readily to the remaining nitrogen atom, so as to produce a symmetrical compound, $PhNH\cdot CS\cdot NHAc$, no tendency to migration has ever been observed where purely hydrocarbon radicles alone are present, as, for example, in $MePhN\cdot CS\cdot NH_2$. Now, the radicle, CO_2Et, is so far electropositive to the acetyl group that it readily expels the latter from $PhNH\cdot CS\cdot NHAc$, whilst the converse action is not realised, even when acetyl chloride in large excess is heated with $PhNH\cdot CS\cdot NH\cdot CO_2Et$ (Doran, Trans., 1896, 69, 343); moreover, in general chemical behaviour, "thiocyanates" containing the group CO_2R (where R = alkyl or aryl) are more akin to ordinary hydrocarbon thiocarbimides than is the case with their fatty acyl congeners. It was of interest, therefore, to learn how the carboxyethyl group, CO_2Et, would comport itself as regards migration.

A quantity of the *aa*-carboxyethylphenyl compound was maintained just at its melting point for half an hour. Little change occurred, save that gas was very slowly evolved, having an odour of mercaptan, and containing carbon dioxide; on raising the temperature to about 160°, this effervescence became vigorous, and, on cooling, a tenacious oil was left, in which nothing could definitely be recognised, except thiocyanic acid and phenylthiocarbimide. Heat led, therefore, not to isomeric change, but to complete disruption of the molecule. Transfer of the acyl group by means of cold weak alkali (Hugershoff's method, *loc. cit.*) could not be effected, the *aa*-compound being insoluble in it and apparently unchanged.

From the results of these and similar experiments, it would seem that an acyl group may usually be attached to the sulphur atom of a monosubstituted thiourea, in the same way as an alkyl group; and that it will remain there so long as, in conjunction with some acid (hydrochloric, picric, or nitric), it can form a salt. On withdrawal of the combined acid, it tends to move to that nitrogen atom which already contains a hydrocarbon radicle; if the acyl group is of pronounced electronegative character, it is prone to move once more, into union with the unoccupied nitrogen atom, to form a symmetrical thiocarbamide, whereas, if the electronegative character is of low degree, this second transfer cannot be accomplished easily, if at all.

There is some reason to believe that, for a short time at least, the free base, $PhNH\cdot C(NH)\cdot S\cdot CO_2Et$, is capable of existence. Thus, when excess of strong alkali was added quickly to the aqueous solution of the hydrochloride, without allowing time for solidification of the precipitate, the latter redissolved at once; the solution had an odour of mercaptan, and, when neutralised with hydrochloric acid, evolved both carbon dioxide and hydrogen sulphide, reacted faintly for aniline, and yielded a precipitate; these changes are probably due, in the main, to a primary decomposition, through the excess of alkali, of the unstable base, $PhNH\cdot C(NH)\cdot S\cdot CO_2Et$, into phenylurea and ethyl thiocarbonic acid, $EtO\cdot CO\cdot SH$, which latter yields (Bender, *Annalen*, 1868, **148**, 137) hydrogen sulphide, mercaptan, &c. The change is complicated through the transformation of a portion of the base into the *aa*-isomeride, for although in some of the experiments ferric chloride gave but a faint reddening of the mixture, yet in no instance was thiocyanic acid entirely absent.

Furthermore, when the precipitate obtained by neutralising the aqueous solution of the hydrochloride was treated at once with hydrochloric acid, it dissolved readily, whereas it has previously been mentioned that, after solidification, this precipitate is practically insoluble in the acid named.

It is possible, of course, that at very low temperature the free base might continue to exist as such, but we had no means of testing this point experimentally.

Concerning the hydrochloride a few details may here be given.

From the alcoholic mixture, prepared as described above, it may conveniently be precipitated by the addition of light petroleum. The resultant mobile clear syrup became temporarily viscid at − 15°, but after half an hour at this temperature showed no sign of solidification. It was rather unstable, bubbles of carbon dioxide beginning to develop after a few hours' standing at the temperature of the room; by warming gently on the water-bath this change was induced at once, the product being the hydrochloride of Bertram's (*loc. cit.*) ethyl ester of iminophenylthiocarbamic acid, $PhNH\cdot C(NH)\cdot SEt$, a mercaptoid substance obtained directly (Dixon, *loc. cit.*) by heating phenylthiourea with ethyl chlorocarbonate in presence of benzene. It is necessary, therefore, in preparing the original hydrochloride to avoid overheating; combination, very slow at the ordinary temperature, occurs rapidly at 35–40°, but a temperature materially higher than this is not permissible.

From the dilute aqueous solution of the hydrochloride the *picrate* separated on the addition of aqueous picric acid, as a bright yellow precipitate, minutely crystalline, very sparingly soluble in cold water, and melting at 85—86°. It was free from chlorine, was desulphurised by a hot alkaline solution of lead or by ammoniacal silver nitrate; on treatment with one equivalent of dilute alkali, and allowing to stand for some minutes, the mixture when heated with strong alkali gave the reaction for thiocyanic acid:

0·4535 gave 0·223 $BaSO_4$. S = 6·8.

$C_{10}H_{12}O_2N_2S,C_6H_3O_7N_3$ requires S = 7·06 per cent.

Ethyl Chlorocarbonate and o-Tolylthiourea.

The additive compound, a clear, mobile, acid syrup, had properties similar to those of the phenylic homologue. It was dissolved in water, and the solution carefully neutralised with dilute caustic alkali. As before, the precipitated oil soon hardened, the solid product, insoluble in water, yielding by crystallisation from alcohol, colourless, flattened prisms, melting at 149—150° with very slight effervescence:

0·238 gave 0·225 $BaSO_4$. S = 13·0.

$C_{11}H_{14}O_2N_2S$ requires S = 13·45 per cent.

Warm, strong caustic alkali readily attacked the crystals, producing an oil which presently changed to a solid; the liquor when acidified reacted intensely with ferric chloride for thiocyanic acid. A *picrate* was obtainable from the hydrochloride, but not from the corresponding "base," which was plainly *aa*-carboxyethyl-*o*-tolylthiocarbamide,

$$C_7H_7N(CO_2Et)\cdot CS\cdot NH_2,$$

isomeric with the *ab*-compound of Doran (*loc. cit.*) melting at 152·5°.

Ethyl Chlorocarbonate and p-Tolylthiourea.

No material difference was found as regards the product in this case and in those already described; the compound, *aa*-carboxyethyl-*p*-tolylthiocarbamide, melted at 146—147°, and yielded thiocyanic acid when attacked by warm caustic potash.

Doran's (*loc. cit.*) *ab*-isomeride melts at 148—149°:

0·238, fused with $NaOH + KNO_3$, gave 0·2334 $BaSO_4$. S = 13·5.

$C_{11}H_{14}O_2N_2S$ requires S = 13·45 per cent.

Phenyl Chlorocarbonate and Phenylthiourea.

Hitherto, the power of phenyl chlorocarbonate to unite with thioureas has been tested in but a single case, Dixon having observed that it can yield a hydrochloride with thiourea (Trans., 1906, **89**, 909). The combination was somewhat unstable, being converted by hot water into carbon dioxide, phenol, and hydrochloric acid, with regeneration of thiourea; its cold aqueous solution, when neutralised with *N*/5 alkali, was decomposed with formation of diphenyl carbonate, and the solid was destroyed by melting, without production of the expected ψ-base, $NH_2\cdot C(NH)\cdot SPh$. Hence the phenylic compound differs markedly in properties from its methylic and ethylic congeners.

On mixing the above constituents, dissolved in acetone, they combined at the ordinary temperature, yielding the hydrochloride in brilliant, white crystals, melting at 115—116° with effervescence; the amount was 76 per cent. of that calculated for a molecular additive product:

0·3085 required 10·1 c.c. *N*/10 $AgNO_3$. Cl = 11·6.

$C_{14}H_{12}O_2N_2S,HCl$ requires Cl = 11·5 per cent.

The substance was decomposed by boiling with water; it dissolved moderately freely in cold alcohol, and the solution, when treated with aqueous picric acid, gave a bright yellow *picrate*. On boiling the solid with an alkaline solution of lead, there was copious desulphurisation; nevertheless, only a portion of the sulphur was thus eliminated, for, on acidifying with hydrochloric acid and treating the clear liquid with ferric chloride, an intense reaction for thiocyanic acid was obtained.

On shaking a cold alcoholic solution of the hydrochloride with excess of calcium carbonate, filtering, and diluting the warm filtrate with water, *aa*-carboxyphenylphenylthiocarbonate crystallised in exceptionally brilliant, pearly leaflets melting at 144—145°:

0·272 gave 0·230 $BaSO_4$. S = 11·6.

$C_{14}H_{12}O_2N_2S$ requires S = 11·77 per cent.

On treatment with hot alkali, droplets of phenylthiocarbimide were precipitated; when this was expelled by boiling and the residual liquid acidified, hydrogen sulphide and carbon dioxide escaped with effervescence, the odour of phenol becoming marked; aniline was present, and ferric chloride gave a strong red coloration. Since the contained sulphur appears both as phenylthiocarbimide and as thiocyanic acid (the hydrogen sulphide possibly originating through the attack of the hot alkali on the former), the interaction must proceed in at least two distinct ways, for example:

(i) $PhCO_2\cdot NPh\cdot CS\cdot NH_2 + H_2O = HSCN + PhOH + CO_2 + PhNH_2$.

(ii) $PhCO_2\cdot NPh\cdot CS\cdot NH_2 + H_2O = PhOH + CO_2 + NH_3 + Ph\cdot NCS$.

This compound is isomeric with the *ab*-derivative,

PhO·CO·NH·CS·NHPh,

of Doran (Trans., 1906, **89**, 343), melting at 148—149°, and yielding with alkali (Dixon, Trans., 1906, **89**, 898) all the products named above with the exception of thiocyanic acid.

o-*Tolyl Chlorocarbonate and Phenylthiourea.*

From the mixed acetone solutions, the hydrochloride was deposited in tufts of colourless prisms, melting with effervescence at 114°:

0·3225 required 10·05 c.c. *N*/10 $AgNO_3$. Cl = 11·1.

$C_{15}H_{14}O_2N_2S,HCl$ requires Cl = 11·01 per cent.

This salt was decomposed by contact with water, and was desulphurised by an alkaline lead solution, even in the cold.

By treating the alcoholic solution with calcium carbonate, evaporating the filtrate to a small bulk, and crystallising the solid residue from alcohol, small, white prisms were obtained, melting without effervescence at 103—104°, and giving with hot caustic alkali reactions similar to those of the corresponding phenylic derivative:

0·286 gave 0·237 $BaSO_4$. S = 11·4.

$C_{15}H_{14}O_2N_2S$ requires S = 11·19 per cent.

This *aa*-compound is isomeric with the *ab*-form, melting at 155—156° (corr.), obtained by Dixon (*loc. cit.*, 1906) from thiocarbimino-*o*-tolylcarbonate and aniline.

p-*Tolyl Chlorocarbonate and Phenylthiourea.*

Vigorous action took place between these constituents in acetone, the mixture quickly changing to a white pulp; the yield of solid product, apart from what remained dissolved in the mother liquor, amounted to 74 per cent. of the theoretical for an additive compound.

The crystalline solid melted with effervescence at 134°, was decomposed by water, and when treated with an alkaline solution of lead, darkened, even in the cold, owing to desulphurisation.

0·3225 required 10·05 c.c. *N*/10 $AgNO_3$. Cl = 11·1.

$C_{15}H_{14}O_2N_2S,HCl$ requires Cl = 11·01 per cent.

On withdrawal of the combined acid by means of calcium carbonate, the base underwent the usual change, yielding *aa*-carboxy-*p*-tolylphenylthiocarbamide, $CH_3·C_6H_4·O·CO·N(C_6H_5)·CS·NH_2$, in long, shining, flattened prisms melting at 133—134°:

0·286 gave 0·227 $BaSO_4$. S = 10·9.

$C_{15}H_{14}O_2N_2S$ requires S = 11·19 per cent.

Hot caustic alkali readily attacked the substance, with precipitation of an oil (phenylthiocarbimide); when this was expelled by boiling, and the residual solution acidified, hydrogen sulphide and carbon dioxide escaped, the liquor developing the characteristic, penetrating odour of *p*-cresol, and reacting strongly for both aniline and thiocyanic acid. This complex decomposition is obviously similar to that of the *aa*-carboxyphenyl homologue, and resembles that of the *ab*-isomeride

$$C_6H_4Me·O·CO·NH·CS·NHPh$$

(Dixon, *loc. cit.*), melting at 157—158° (corr.), in every respect, save that the latter yields no thiocyanic acid.

Phenyl Chlorocarbonate and o-*Tolylthiourea.*

The yield of additive compound, prepared in warm acetone solution, reached 92 per cent. of that calculated, the product being a white, crystalline solid melting, when quickly heated, at 98—99° with effervescence:

0·3225 required 9·95 c.c. $N/10$ $AgNO_3$. Cl = 10·95.

$C_{15}H_{14}O_2N_2S,HCl$ requires Cl = 11·01 per cent.

By treatment of the alcoholic solution with calcium carbonate, the *aa*-compound was obtained in brilliant, long, vitreous prisms, melting at 119—120°, and yielding with caustic alkali, *o*-tolylthiocarbimide, phenol, thiocyanic acid, &c.:

0·286 gave 0·2324 $BaSO_4$. S = 11·2.

$C_{15}H_{14}O_2N_2S$ requires S = 11·19 per cent.

This product is another isomeride of the *aa*-compound melting at 103—104° already described.

Phenyl Chlorocarbonate and p-*Tolylthiourea.*

Nearly 70 per cent. of the calculated yield of hydrochloride was precipitated from the mixed acetone solutions; the salt occurring as a white, crystalline solid which melted, when rapidly heated, at 108° with effervescence. The melting points of all these hydrochlorides are influenced largely by the rate of heating, a phenomenon which is doubtless conditioned by the gradual loss, with increasing temperature, of hydrogen chloride:

0·3225 required 9·75 c.c. $N/10$ $AgNO_3$. Cl = 10·7.

$C_{15}H_{14}O_2N_2S,HCl$ requires Cl = 11·01 per cent.

Elimination of the combined haloid acid by means of calcium carbonate in the cold, furnished a solid, which, after crystallisation from alcohol, formed large, brilliant, flattened prisms melting at 153° and giving the reactions of an *aa*-derivative:

0·286 yielded 0·2324 $BaSO_4$. S = 11·2.

$C_{15}H_{14}O_2N_2S$ requires S = 11·19 per cent.

This substance, *aa*-carboxyphenyl-*p*-tolylthiocarbamide, constitutes the third strict representative of its class, being a pure position-isomeride of the *aa*-carboxy-*p*-tolylphenylthiocarbamide, of m. p. 133—134°, previously described, and of the corresponding *ab*-compound (see above).

When treated with hot alkali it decomposes with formation of *p*-tolylthiocarbimide, phenol, thiocyanic acid, &c.

Palmityl Chloride and Thiourea.

On mixing these constituents, dissolved in cold acetone, a copious, white precipitate separated, consisting of the hydrochloride,

$$NH_2\cdot C(NH)\cdot S\cdot CO\cdot C_{15}H_{31},HCl\ ;$$

it was apparently insoluble in cold water, melted at 111—113°, and gave, when treated in alcoholic solution with alcoholic picric acid, a bright yellow *picrate*:

0·3505, fused as before, required by Volhard's method 9·9 c.c. *N*/10 $AgNO_3$. Cl = 10·0.

0·3505 gave 0·226 $BaSO_4$. S = 8·9.

$C_{17}H_{35}ON_2ClS$ requires Cl = 10·13; S = 9·12 per cent.

Boiling water decomposed the hydrochloride with formation of an oil which solidified on cooling. The liquor, when evaporated, left a white, crystalline solid, containing thiocarbamidic sulphur, and yielding with ethyl nitrite and ferric chloride, Claus' reaction (*Annalen*, 1876, **179**, 129) for thiourea; the solidified oil, when crystallised from dilute alcohol, separated in greasy crystals, free from chlorine, nearly free from sulphur, giving a soap with caustic alkali, and melting at 64°; this was obviously palmitic acid (m. p. 62°), containing a trace of impurity.

The reaction with water is therefore similar to that in the case of the acetyl homologue, $NH_2\cdot C(NH)\cdot S\cdot COMe,HCl$, Dixon and Hawthorne (*loc. cit.*).

Palmityl Chloride and Phenylthiourea.

From the mixed acetone solutions the hydrochloride was deposited as a bulky, snow-white precipitate melting at 64—65°:

0·4265, fused with $NaOH + KNO_3$, required 9·8 c.c. *N*/10 $AgNO_3$. Cl = 8·16.

0·4265, fused with $NaOH + KNO_3$, gave 0·232 $BaSO_4$. S = 7·5.

$C_{23}H_{39}ON_2ClS$ requires Cl = 8·32; S = 7·50 per cent.

Hence the product was a molecular additive compound.

When allowed to stand in contact with strong caustic alkali, the solid was attacked, the mixture, when acidified, giving with ferric chloride a strong reaction for thiocyanic acid, and thereby showing the presence of *aa*-palmitylphenylthiocarbamide,

$$C_{15}H_{31}CO{\cdot}NPh{\cdot}CS{\cdot}NH_2.$$

This compound was isolated by means of calcium carbonate, and, when recrystallised from weak alcohol, formed long needles melting at about 74°; with caustic alkali, it yielded thiocyanic acid, and hence was isomeric with the *ab*-form, produced (Dixon, Trans., 1896, **69**, 1595) from palmitylthiocarbimide and aniline, and melting at 62—63°:

0·390 gave 0·225 $BaSO_4$. S = 7·9.

$C_{23}H_{38}ON_2S$ requires S = 8·18 per cent.

By heating, it is readily converted into the *ab*-isomeride.

Phenylacetyl Chloride and Thiourea.

Using acetone solutions, snow-white, odourless, flattened prisms were obtained, the yield amounting to more than 90 per cent. of that calculated from the equation:

$$CH_2Ph{\cdot}COCl + NH_2{\cdot}C(NH){\cdot}SH = NH_2{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}CH_2Ph,HCl.$$

0·461, fused with $NaOH + KNO_3$, required 19·3 c.c. *N*/10 $AgNO_3$. Cl = 14·9.

0·407, fused with $NaOH + KNO_3$, gave 0·409 $BaSO_4$. S = 13·8.

$C_9H_{10}ON_2S,HCl$ requires Cl = 15·40; S = 13·88 per cent.

The hydrochloride melted at 81—82°; by dissolution in hot water it was almost completely decomposed into hydrochloric acid, phenylacetic acid, and thiourea:

0·2305, dissolved in a little hot water, required for neutralisation 18·5 c.c. *N*/10 KOH, but on diluting to about 500 c.c. 19·8 c.c. were required, the calculated amount for two equivalents being 20 c.c.

By dropping a freshly-prepared, concentrated solution into aqueous picric acid, a bright, orange-yellow *picrate* was obtained in fine needles, free from chlorine, and melting at 107—108° with decomposition; this salt is dissociated by hot water.

Phenylacetyl Chloride and Phenylthiourea.

The constituents united vigorously in warm acetone; by recrystallisation from this solvent the product was obtained as a bulky, snow-white solid melting at 130—131°:

0·542, fused with NaOH, &c., required 17·9 c.c. *N*/10 $AgNO_3$. Cl = 11·7.

0·3065 gave 0·2292 $BaSO_4$. S = 10·3.

$C_{15}H_{14}ON_2S,HCl$ requires Cl = 11·58; S = 10·44 per cent.

The hydrochloride was soluble in alcohol, nearly insoluble in cold water, but apparently decomposed by it, the mixture yielding no reaction for thiocyanic acid. By contact with strong caustic alkali it was readily attacked, with formation of thiocyanic acid, and hence with production of *aa*-phenylacetylphenylthiocarbamide; the *ab*-compound when thus treated yields no thiocyanic acid.

The *aa*-derivative was isolated by shaking a cold alcoholic solution of the hydrochloride with excess of calcium carbonate, the filtrate, on spontaneous evaporation yielding beautiful, vitreous, rhombic crystals. These were freed from a trace of phenylthiourea by treatment with cold chloroform, in which the latter is practically insoluble; on evaporating the solvent and crystallising the residue from alcohol, long, colourless prisms were obtained melting at 113—114° (corr.):

0·27 gave 0·2352 $BaSO_4$. S = 12·0.

$C_{15}H_{14}ON_2S$ requires S = 11·86 per cent.

The product was insoluble in water, moderately soluble in hot alcohol, and freely so in chloroform. It was desulphurised imperfectly by boiling with alkaline lead tartrate, and when heated with alkali yielded a turbid mixture reacting strongly for thiocyanic acid, consequently it is isomeric with the *ab*-phenylacetylphenylthiocarbamide, $CH_2Ph\cdot CO\cdot NH\cdot CS\cdot NHPh$, of m. p. 109—110°, obtained by Dixon (Trans., 1896, **69**, 866) from phenylacetylthiocarbimide and aniline.

Action of Heat on aa-*Phenylacetylphenylthiocarbamide.*—A quantity was melted and kept for two hours at 110°. No effervescence occurred, and the loss of weight was immaterial (less than 0·5 per cent.); the cooled fusion, a resin, was dissolved in cold chloroform, the solution after spontaneous evaporation leaving a white solid, which on crystallisation from alcohol separated in tufts of lustrous, white prisms, containing thiocarbamidic sulphur, but giving no reaction for thiocyanic acid when treated with hot alkali. Its mixture with the original *aa*-compound melted indistinctly between 90° and 102°; on the other hand, when three tubes, charged respectively with (1) the above substance, (2) a specimen of *ab*-phenylacetylphenylthiocarbamide, prepared from the corresponding thiocarbimide and aniline, and (3) a mixture in equal parts of (1) and (2) were attached to the same thermometer, they all melted sharply at the same moment at 109—110° (corr.). Consequently, the product was *ab*-phenylacetylphenylthiocarbamide.

Now the original hydrochloride, when treated with picric acid, yields a picrate and hence contains a basic form, whilst neither the *aa*- nor the *ab*-derivative reacts with picric acid. The phenylacetyl group, therefore, primarily attached to sulphur, leaves it when the base is liberated at the ordinary temperature, and passes to the phenylated nitrogen atom, yielding a compound stable enough to admit of crystallisation from boiling alcohol, but undergoing a second transposition at its melting point: $PhNH{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}CH_2Ph,HCl \longrightarrow PhCH_2{\cdot}CO{\cdot}NPh{\cdot}CS{\cdot}NH_2 \longrightarrow PhCH_2{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$.

Phenylbenzylcarbamic Chloride and Phenylthiourea.

In a recent paper (Dixon and Hawthorne, *loc. cit.*) it was shown that disubstituted carbamic chlorides, when heated with thiourea, yield molecular additive compounds, the hydrochlorides of bases, $NH_2{\cdot}C(NH){\cdot}S{\cdot}CO{\cdot}NXY$, the nitrates and picrates of which are sufficiently stable to allow of their being recrystallised from boiling water. The bases, however, being attacked with great ease by dilute alkali were not isolated; they are isomeric with certain thiobiurets of the form, $NXY{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2$, prepared by Dixon (Trans., 1899, **75**, 388) from disubstituted carbamylthiocarbimides and ammonia. It remained now to be learned whether substituted thioureas also would unite with these carbamic chlorides.

Phenylbenzylcarbamic chloride and phenylthiourea were selected for experiment.

Unsatisfactory results were obtained on fusing the constituents together directly; the chloride was therefore dissolved in benzene and the solution heated with one molecular proportion of the thiourea, using a reflux condenser; in these circumstances carbonyl sulphide was evolved and a pasty solid left. By means of acetone this was separated into benzylaniline hydrochloride and a tenacious syrup, almost free from sulphur, and consisting probably of phenylcyanamide, $BzPhN{\cdot}COCl + PhNH{\cdot}C(NH){\cdot}SH = BzPhNH,HCl + COS + PhNH{\cdot}CN$.

This unexpected result, namely, desulphurisation of the thiourea, recalls a somewhat analogous change observed with phenylmethylcarbamic chloride and thiocarbanilide; these substances, when gently heated together, decomposing with evolution of carbonyl sulphide and production of phenylthiocarbimide, together with the hydrochloride of triphenylguanidine (*loc. cit.*, 405).

The previous experiment was repeated by heating phenylbenzylcarbamic chloride and phenylthiourea with acetone for some days at 40—45°, but although interaction took place, no additive compound could be isolated from the viscid reaction product.

In the paper by Dixon and Hawthorne, cited above, is mentioned the failure of attempts to prepare from the hydrochloride,

$$PhN{\cdot}C(NH){\cdot}S{\cdot}COPh,HCl,$$

the *aa*-derivative, $PhN(COPh){\cdot}CS{\cdot}NH_2$.

That this substance existed in the material left on elimination of the combined halogen acid was inferred from the fact that after treatment with caustic alkali it yielded the reaction for thiocyanic acid. Yet on recrystallisation the only product which separated was the *ab*-compound, the mother liquor giving an enfeebled thiocyanic reaction with potash; the solid residue, obtained by evaporating this liquor when again crystallised, yielded more of the *ab*-derivative, but the solution now gave practically no thiocyanic reaction with alkali.

As a reason for the gradual extinction of the power of yielding thiocyanic acid, it was conjectured that the benzoyl group might possess so free a mobility that the mere warming necessary for recrystallisation might be sufficient to cause its transference from the phenylated to the non-substituted nitrogen atom, thus:

$$\mathrm{PhN(COPh){\cdot}CS{\cdot}NH_2} \longrightarrow \mathrm{PhNH{\cdot}CS{\cdot}NH(COPh)};$$

at the time it was not possible to test this experimentally.

In dealing with this hydrochloride, whether the halogen acid was removed by sodium ethoxide or by calcium carbonate (both methods were tried), the salt was previously dissolved in nearly absolute alcohol which effected considerable dissociation (into benzoic acid, hydrochloric acid, and phenylthiourea), and hence it was necessary to separate these by-products from the *aa*-compound formed, a process obviously both circuitous and wasteful. With the view of achieving more directly the production of the substance required, we now had recourse to Hugershoff's method, namely, interaction of the thiourea and the acid anhydride.

Benzoic Anhydride and Phenylthiourea.

When phenylthiourea was heated on the water-bath with a slight excess of benzoic anhydride until the mixture became clear, the product (which at first gave the thiocyanic reaction), after two recrystallisations from alcohol, formed vitreous prisms melting at 145—146° (uncorr.); these gave no trace of thiocyanic acid with caustic alkali, and consisted no doubt of *ab*-benzoylphenylthiocarbamide, $\mathrm{COPh{\cdot}NH{\cdot}CS{\cdot}NHPh}$.

Benzoic Anhydride and p-*Tolylthiourea.*

It being evident from the last result that if an *aa*-compound had been formed at all the benzoyl group must then have changed its position, the experiment was repeated at a lower temperature. Moreover, as in the previous experiments (*loc. cit.*), attempts to prepare a hydrochloride from phenylthiourea had been unsuccessful, the hydrochloride actually obtained being that derived from *p*-tolylthiourea, the latter was now selected for examination.

In the first test, *p*-tolylthiourea was heated with benzoic anhydride at 80°; in about ten minutes the mixture began to give the reaction with caustic alkali for thiocyanic acid; it did not clear, however, and after a little more than an hour the pasty, brown melt was crystallised from alcohol. The material deposited gave no thiocyanic reaction, and consisted of pure *ab*-benzoyl-*p*-tolylthiocarbamide; the liquor from this gave the reaction, but on concentration yielded only the *ab*-compound.

The trial was repeated at a temperature not exceeding 60°; in these circumstances interaction occurred slowly and imperfectly, the semi-fused product giving the thiocyanic reaction for an *aa*-compound. But, as before, the only substance which could definitely be isolated was *ab*-benzoyl-*p*-tolylthiocarbamide. From those results it would appear that the *aa*-compound is formed by the interaction of the constituents named, but that at the temperature of this reaction considerable change occurs in the *ab*-form, and that by recrystallisation from alcohol the same change is easily completed. It is curious that the benzoyl group, in spite of a relatively high combining weight, should exhibit mobility in a much higher degree than acetyl, propionyl, &c.

For convenience and in order to collect the somewhat scattered literature of the subject, a list is subjoined of the basic acyl-ψ-thiourea forms now known as salts, and of their isomerides, the acylthioureas, together with the respective melting points and references to original papers.

Table I includes the hydrochlorides of acyl-ψ-thioureas,

$$NH_2{\cdot}C(NH){\cdot}SR,$$

TABLE I.—*Monosubstitution Derivatives.*

Acyl-ψ-thiourea (hydrochloride).	Melting point.	Observer and reference.	M. p. of acylthiourea.	Observer and reference.
Acetyl, $CH_3{\cdot}CO$	109°	C. D. and H.	165°	N. and L.
Palmityl, $C_{15}H_{31}{\cdot}CO$	111—113°	D. and T.	—	—
Phenylacetyl, $PhCH_2{\cdot}CO$	82°	,,	—	—
Benzoyl, PhCO	116	D. and H.	170	Pk.
Carboxymethyl, $MeO{\cdot}CO$	90	D. (i)	166	Do. (i)
Carboxyethyl, $EtO{\cdot}CO$	117	Pl., D. (i)	140	Do. (ii)
Carboxyphenyl, $PhO{\cdot}CO$	130	D. (ii)	175 (corr.)	D. (ii)
Diphenylcarbamyl, $Ph_2N{\cdot}CO$	183	D. and H.	183 (corr.)	D. (iii)
Phenylmethylcarbamyl, $MePhN{\cdot}CO$	About 175	,,	167 (corr.)	,,
Phenylethylcarbamyl, $EtPhN{\cdot}CO$	160	,,	148 (corr.)	,,

and the corresponding acylthioureas, $NHR{\cdot}C(NH){\cdot}SH$ (where R represents the acyl group).

Table II comprises disubstitution isomerides of the form (i) $NHX{\cdot}C(NH){\cdot}SR,HCl$, (ii) $NXR{\cdot}CS{\cdot}NH_2$, and (iii) $NHR{\cdot}CS{\cdot}NHX$ (where X indicates a hydrocarbon radicle and R, as before, an acyl group).

TABLE II.—*Disubstitution Derivatives.*

Groups included.		(i).		(ii).		(iii).	
R.	X.	M. p. of acyl-ψ-form (hydrochloride).	Observer and reference.	M. p. of *aa*-form.	Observer and reference.	M. p. of *ab*-form.	Observer and reference.
Acetyl	Phenyl	94°	D. and H.	139°	Hu.	173°	M. (i), S.
,,	*o*-Tolyl	96	,,	140	,,	184	D. (iv)
,,	*p*-Tolyl	103	,,	137	,,	176	M. (ii)
Palmityl	Phenyl	65	D. and T.	74	D. and T.	63	D. (v)
Benzoyl	*p*-Tolyl	138	D. and H.	—	—	159	M. (i), D. and H.
Phenylacetyl	Phenyl	131	D. and T.	114 (corr.)	D. and T.	110	D. (vi)
Carboxymethyl	Phenyl	87	D. (i)	167 (corr.)	D. (i)	158	Do. (i)
,,	*o*-Tolyl	93	,,	176 (corr.)	,,	172	,,
,,	*p*-Tolyl	solid	,,	176 (corr.)	,,	158	,,
Carboxyethyl	Phenyl	syrup	D. and T.	133	D. and T.	130	Do. (ii)
,,	*o*-Tolyl	,,	,,	150	,,	152·5	,,
,,	*p*-Tolyl	,,	,,	147	,,	149	,,
Carboxyphenyl	Phenyl	116°	,,	145	,,	149	Do. (iii)
,,	*o*-Tolyl	99	,,	120	,,	165 (corr.)	D. (ii)
,,	*p*-Tolyl	108	,,	153	,,	145 (corr.)	,,
Carboxy-*o*-tolyl	Phenyl	114	,,	104	,,	156 (corr.)	,,
Carboxy-*p*-tolyl	Phenyl	134	,,	134	,,	158 (corr.)	,,

C. = Claus, *Ber.*, 1875, **8**, 42; D. (i) = Dixon, Trans., 1903, **83**, 550; D. (ii) = Trans., 1906, **89**, 892; D. (iii) = Trans., 1899, **75**, 388; D. (iv) = Trans., 1889, **55**, 304; D. (v) = Trans., 1896, **69**, 1595; D. (vi) = Trans., 1896, **69**, 866; D. and H. = Dixon and Hawthorne, Trans., 1907, **91**, 122; D. and T. = Dixon and Taylor, this paper; Do. (i) = Doran, Trans., 1901, **79**, 906; Do. (ii) = Trans., 1896, **69**, 324; Do. (iii) = Trans., 1905, **87**, 343; Hu. = Hugershoff, *Ber.*, 1899, **32**, 3649; M. (i) = Miquel, *Ann. Chim. Phys.*, 1877, [v], **11**, 318; M. (ii) = *Bull. Soc. chim.*, 1877, [ii], **28**, 103; N. and L. = Nencki and Leppert, *Ber.*, 1873, **6**, 905; Pk. = Pike, *Ber.*, 1873, **6**, 755; Pl. = Pawlewski, *Ber.*, 1888, **21**, 402; S. = R. Schiff, *Ber.*, 1876, **9**, 570.

Conclusions.

Although the number of cases hitherto examined is not sufficient to warrant the laying down of general principles, still the following appear to hold, and, pending further observation, are here advanced provisionally.

(1) All definitely acid chlorides containing the group ·COCl, united to a hydrocarbon radicle, either directly or through the intervention of an oxygen atom, combine with thiourea or its non-acidic monosubstitution derivatives, yielding in each case the hydrochloride of a *pseudo*-form,

$$NH_2{\cdot}C(NH){\cdot}S{\cdot}COR,$$

where R represents the hydrocarbon or oxyhydrocarbon radicle.

(2) Where R is aliphatic in general character, the withdrawal of the combined acid leads to the formation of the corresponding base, which at the ordinary temperature is unstable, the acyl group leaving the molecule, if this is non-substituted (that is, derived from thiourea); but if it is substituted, then migrating, in a short time, but not necessarily at once, to that nitrogen atom united with the substituting group, to form an *aa*-disubstituted thiourea or thiocarbamide. The latter is of moderate stability, but changes again when melted, the acyl radicle now passing into union with the nitrogen atom previously non-substituted to yield a symmetrical disubstituted thiocarbamide. In other words, a certain thiourea molecule may exist successively in three forms, namely (see Trans., 1895, 67, 564), (i) acyl-ψ-ν-arylthiourea, (ii) ν-acylarylthiourea (or *aa*-acylarylthiocarbamide), and (iii) *a*-acyl-*b*-arylthiocarbamide.

(3) Where R = phenyl, the form (ii) above represents a stage of low stability, the product, on very slight rise of temperature, passing into form (iii).

(4) Where R is united to CO through an oxygen atom, the whole group RO·CO· becomes electropositive (as compared with R·CO·); in these circumstances the withdrawal of hydrochloric acid from the hydrochloride $XNH{\cdot}C(NH){\cdot}S{\cdot}CO_2R,HCl$ leads as before to the production of the above form (ii), but with this increasing basicity of the "acyl" group its resistance to transfer becomes more marked, the compound, when cautiously fused, undergoing but little change; if the temperature is raised, disruption of the molecule occurs.*

(5) If the "acyl" group be of the comparatively basic form, XYN·CO· (where X and Y are purely hydrocarbon radicles), the compound XYN·COCl can yield a hydrochloride with thiourea, but

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* Distinctly electropositive groups, namely, hydrocarbon radicles, are not known to undergo movement from the *aa*- to the *ab*-form in thiocarbamides.

hitherto no similar compound has been obtained with its substitution derivatives; moreover, the products with thiourea itself are decomposed readily with formation of the secondary amine corresponding to the disubstituted carbamic chloride.

It is proposed to extend the study of these combinations so as to include other classes both of acylogens and of substituted thiocarbamides.

QUEEN'S COLLEGE,
CORK.

LXXXVI.—*The Chemical Action of the Radium Emanation. Part I. Action on Distilled Water.*

By Sir WILLIAM RAMSAY, K.C.B., F.R.S.

THE emanation from radium is one of the most potent, if not the most potent chemical agent which exists in nature. Of all known substances it is endowed with the greatest content of potential energy: for one cubic centimetre contains, and can evolve, nearly three million times as much heat as an equal volume of a mixture of two volumes of hydrogen with one of oxygen. The spontaneous change which it undergoes, moreover, is accompanied by the emission of an immense number of corpuscles, expelled with a velocity approaching that of light in magnitude, and which have a remarkable influence on matter. For some years I have been engaged in studying its chemical action, and in this memoir I shall attempt to describe its action on pure water.

Since the discovery of this gas by Dorn in 1900, it has been the subject of many researches, physical for the most part. What we know of its properties can be told in a few words.

It is a gas of unknown, but probably considerable density (Rutherford and Miss Brooks, *Trans. Roy. Soc. Canada*, 1901), which unceasingly escapes from salts of radium, preferably dissolved in water. Its most remarkable property is its spontaneous change into helium (Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 204, and 1904, **73**, 346) and other products (radium *A*, *B*, *C*, &c.); the latter also possess a limited life; it is supposed that radium *F* is identical with polonium. The emanation obeys Boyle's law; its spectrum was examined by Ramsay and Collie (*ibid.*, 1904, **73**, 470). Attempts have been made to determine its density by measuring its rate of diffusion, and so to gain knowledge of its molecular weight; the results of such experiments are somewhat unsatisfactory, but appear to indicate a density of about 100, and a consequent molecular weight of about 200. It resists attack by all chemical agents which have been tried; like argon and its congeners, it is unaffected by sparking with oxygen in presence of caustic potash or by prolonged contact with a red hot mixture of magnesium dust and lime; it would therefore appear to belong to the helium group of elements. If this be so, its atomic weight and its molecular weight should be identical, for its molecule is probably monatomic. Perhaps its atomic weight is approximately 216·5, for the mean difference between five pairs of elements, of which one example is tin and lead, is 88·5; and this number, added to the atomic weight of xenon, 128, gives 216·5. The number 216·5 would correspond approximately to a density of 100.

It can be condensed by cooling it to −185° by means of liquid air (Rutherford and Soddy, *Phil. Mag.*, 1903, [vi], **5**, 561). Rutherford and Soddy state that it is non-volatile at temperatures a few degrees below 150°; but it must certainly possess a vapour pressure even at −185°, for when a complete vacuum is made over the frozen emanation, in pumping off other gases, luminous bubbles travel down the fall-tube of the Töpler pump.

It emits only α-rays; and its rate of half-decay is 3·71 days (Rutherford), 3·99 (Curie), and 3·86 (Sackur). The Curies discovered that radium continually evolves heat; and Rutherford has shown that the major part of the heat is due to the disintegration of the emanation; the emanation given off by a gram of radium in an hour evolves about 75 calories. This heat owes its origin, not only to the disintegration of the emanation, but also to the spontaneous change of several of its products. The total heat evolved during the life of a cubic centimetre of emanation is close on 7 million gram-calories. Now, the heat evolved on explosion of a cubic centimetre of a mixture of hydrogen and oxygen in theoretical quantity is about 3 calories; it follows that during its disintegration the emanation emits nearly 2½ million times as much heat as that of an equal volume of hydrogen and oxygen combining with explosion to form water.

It was with the design of applying this enormous store of energy that the experiments about to be chronicled were begun, about two years ago. The quantity of radium at my disposal has varied from time to time, for it was in use for other experiments.

1. *The Evolution of Heat by the Radium Emanation.*—Although Rutherford has made a quantitative estimation of the amount of heat evolved from the emanation, a qualitative confirmation will here be given; any confirmatory evidence has some value.

Two thermometers were constructed; one, an ordinary thermometer, the scale of which registered tenths of degrees; the bulb of the other was hollow, so that a quantity of the emanation, mixed with hydrogen, could be introduced into a chamber surrounded by the mercury of the thermometer. The two thermometers were carefully compared. They were placed, after filling the hollow bulb of the one with the emanation obtained in five days from 162 milligrams of radium bromide, in two silvered vacuum vessels, and they rested in cotton-wool, with which the vacuum vessels were lightly packed. These vessels were placed side by side in a room of which the temperature remained nearly constant. The following table gives the differences between the two temperatures; needless to say, that of the thermometer containing the emanation was the higher:

Date—Nov.	20.	21.	22.	23.	24.	25.	26.	27.	28.	29.	30.
Difference	0·52°	0·73°	0·63°	0·53°	0·48°	0·34°	0·25°	0·23°	0·19°	0·16°	0·13°

Date—Dec....	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Difference ...	0·13°	0·13°	0·12°	0·10°	0·0°	−0·01°	−0·03°	+0·03°	−0·01°	+0·02°

These figures show incontestably that the emanation evolves heat during its change, and that the amount liberated decreases from day to day.

2. *The Relative Amounts of Oxygen and Hydrogen Evolved, along with Emanation, by the Action of Radium Bromide on Water.*—Giesel (*Ber.*, 1902, **35**, 360; also 1903, **36**, 347) was the first to observe this decomposition; Bodländer found the gaseous mixture to contain 12 per cent. of oxygen and 88 per cent. of hydrogen; the excess of hydrogen was 64 per cent. Later, Ramsay and Soddy (*loc. cit.*) found 29·8 per cent. of oxygen and 70·2 per cent. of hydrogen; the excess of hydrogen is 10·6 per cent. Whence comes this excess? They ascribe it to the oxidation of the grease of the stopcock; but that danger was avoided in the work of which an account will be given. The following experiments were made in the hope of solving this problem.

The first question to be answered was: Does radium bromide evolve gas when dissolved? A very pure sample of bromide, bought from Büchner & Co., of Brunswick, was employed. It is worth noting that five samples of bromide, bought from that firm at different times, all had the same relative discharging power on an electroscope, as measured by the β-rays evolved, and the natural conclusion is that they all possessed the same degree of purity. The volume of the gas obtained from the sample used (which weighed 50 milligrams), on dissolving it in water, was 0·1444 c.c.; after explosion the volume was 0·0477 c.c.; the residue consisted solely of hydrogen, mixed with a trace of helium, the latter detected by its spectrum. Now, crystalline bromide probably contains two molecules of water, which should be resolved into oxygen and hydrogen by the action of the radium. The excess of hydrogen is 33 per cent., and it must be supposed that the gases were occluded by the bromide and liberated on its being dissolved.

The next experiments, made at considerable intervals of time, show the yield of "electrolytic gas," with the excess of hydrogen, obtained from varying amounts of radium bromide:

	Weight of $RdBr_2,2H_2O$ gram.	Time of collection in hours.	Volume of gas in c.c.	Volume per gram per 100 hours in c.c.	Excess of hydrogen per cent.
1.	0·0600	96½	1·67	28·0	14·50 *
2.	0·0600	168	2·88	28·6	4·44
3.	0·1090	240	8·91	34·0	3·65
4.	0·1090	196½	6·86	32·1	13·90 *
5.	0·1090	336	16·43	44·9	6·13
6.	0·0700	192	2·57	19·1	16·00 *
7.	0·1000	168	5·09	30·3	3·76
8.	0·1000	168	4·93	29·3	7·23
9.	0·1620	48	3·18	41·8	7·83
				Mean 32·0	Mean 5·51

* The quantities marked with an asterisk had remained in contact with mercury for a night, before being measured. They have been omitted in taking the mean.

The inequality in these results may be accounted for by several considerations. First, the emanation is soluble in water, and it decomposes water; hence, if the gases remain in contact with the solution, more water is decomposed than if they are removed by the pump shortly after their liberation. Second, the emanation causes recombination of hydrogen and oxygen at a rate which depends on the amount present, and probably on the temperature. Third, the emanation causes oxygen to attack mercury when they are left in contact. The following special experiment illustrates this fact.

The initial volume of a mixture of emanation with pure oxygen was 2·13 c.c.; after being kept for five days over mercury it had decreased to 1·97 c.c., and the surface of the mercury had become coated with a white deposit, which gradually changed to red, and appeared to consist of mercuric oxide. A similar experiment with hydrogen left the surface of the mercury undimmed.

For these experiments on the volume of "electrolytic" gas produced by the emanation, the radium bromide was dissolved in water in little bulbs, sealed to a common tube connected with a Töpler pump. To prevent possible leakage, after each removal of gas the reservoir of the pump was raised so as to cause the mercury to leak past the valve and to pass a stop-cock closing the tube connected with the bulbs; the gases were thus confined by mercury and did not come into contact with the grease of the stop-cock. The entrance tube to the pump was capillary, and so the surface of contact of gas and mercury was very small; the excess of hydrogen cannot be ascribed to the attack of the mercury. Even in experiments 1, 4, and 6, when the gases remained for a night in contact with a large surface of mercury in the collecting tube, of 1·5 cm. diameter, the mercury was not much attacked. The arrangement prevented the attack of the grease by the oxygen in presence of emanation; before it was adopted, carbon dioxide was always detected spectroscopically, but after its adoption none was present.

To account for the excess of hydrogen, several hypotheses may be suggested. It is conceivable that hydrogen may be one of the products of disintegration of radium; but it is very improbable that it should be formed in such large amount. An experiment may be cited here which bears on the subject. A bulb containing 17 milligrams of radium bromide was sealed to the pump. The colour of the bromide was chocolate-brown, but some hours after a vacuum had been made its colour changed to white, and it appeared to have dried. After standing for a day, a little gas was pumped off; it did not explode on passing a spark, but after it had been mixed with half its volume of oxygen, a spark caused explosion, and there was no visible residue. Some days later, a second bubble was extracted: when introduced into a vacuum-tube, it showed the spectrum of hydrogen; a week later no gas could be pumped off.

It is well known that minerals containing thorium and uranium always contain helium (Ramsay and Travers, *Proc. Roy. Soc.*, 1897, 62, 328); and some months after the discovery of helium an attempt was made to ascertain whether the helium existed in a state of combination with one of the constituents of the mineral. Several experiments were made in which the mineral was heated with hydrochloric or sulphuric acid, and the ratio of the hydrogen to the helium in the liberated gas was determined. The problem, however, was complicated by the fact that ores of uranium always contain that element as UO_3, which is reducible by hydrogen to UO_2; it would otherwise be possible to deduce the valency of helium. An imaginary example will make this conception clear. Suppose that ammonia were so unstable that immediately on its liberation it were to decompose into hydrogen and nitrogen. If it were required to determine the valency of nitrogen in magnesium nitride, the action of water, which actually liberates ammonia, would, under the supposed conditions, yield a mixture of one volume of nitrogen with three of hydrogen. The absorption of the hydrogen by a reducible agent would prevent the accuracy of such an experiment.

Our knowledge of the transformation of radium emanation into helium alters the problem. It is no longer likely that helium is contained in the mineral in a state of combination; it is almost certain that the gas is distributed through the mineral in a molecular condition, having been formed *in situ* owing to the disintegration of the radium in the uraninite; or possibly owing to the disintegration of the uranium itself, though we do not know whether helium is one of the products of the disintegration of uranium. Still, it must be noted that if α-rays consist of helium, they are emitted during the change of uranium into uranium *X*.

Returning to the question—Is hydrogen one of the products of the disintegration of the emanations of radium and thorium? some help may be gained by considering thorianite, the cubical mineral from Ceylon. It contains little reducible oxide, and when heated or dissolved it yields a relatively large amount of helium. It has been found, and will be described in a subsequent paper, that thorium nitrate from thorianite probably yields helium on standing, and Debierne has shown that helium is also one of the products of disintegration of actinium. Now thorianite, heated in a vacuum with sulphuric acid diluted with its own volume of water, gives very little, if any, hydrogen. From 1·3779 grams of the mineral, I obtained 8·37 c.c. of gas, after removal of carbon dioxide; oxygen was added, and sparks were passed for half an hour; after removal of the oxygen with phosphorus, the residue, measuring 8·05 c.c., consisted of pure helium; the volume of the hydrogen was therefore 0·32 c.c., or 0·23 c.c. per gram; the atomic proportion would be one atom of hydrogen to thirteen of helium.

In a second experiment, where the thorianite was fused with sodium hydrogen sulphate, a mixture of sulphur dioxide, oxygen, and helium was obtained. Part of the sulphur dioxide owes its origin to the decomposition of sulphuric anhydride; by estimating the oxygen, calculating it to sulphur dioxide, and subtracting that quantity from the total sulphur dioxide, the remainder, 16·34 c.c., was evidently produced by the oxidising action of sulphuric acid on the U_3O_8, which was transformed into $3UO_3$, and on the $2FeO$, converted into Fe_2O_3; this would have required 16·30 c.c. of sulphur dioxide. It may be stated, therefore, that hydrogen is probably not one of the products of the disintegration of thorium, and, from analogy, a similar conclusion may be drawn as regards radium bromide.

The hydrogen pumped off from the solid radium bromide is in all probability derived from the water of crystallisation of the salt. But the question still remains unanswered—whence arises the excess of hydrogen? What becomes of the oxygen?

A second possibility is that the radium bromide is decomposed into metallic radium (which would attack the water and yield hydrogen) and into bromine (this suggestion has been made, indeed, by Giesel); and bromine is easy to identify. Or, again, it may be suggested that ozone is a product of the action of radium on water, and consequently the initial volume would be too small. But ozone, like oxygen, explodes quantitatively with hydrogen, so that its presence would not account for the excess of hydrogen.

To test these suppositions, the following experiment was made. A bulb containing 70 milligrams of radium bromide, dissolved in water, was sealed to a small U-tube containing a faintly acid solution of potassium iodide and starch. During seven days, bubbles of gas passed through this solution, but no blue colour was seen, even on heating the bulb, so as to expel any trace of bromine which might have been liberated. This would also exclude ozone. It has been remarked that the odour of ozone may be perceived on opening a capsule containing radium bromide; I have opened many capsules, and I have never noticed this. Moreover, an experiment which has been in progress for more than two years negatives the supposition. The gases from 212 milligrams of radium bromide have been removed every two or three days by means of a Töpler pump. The mercury shows no trace of ozonide; it is absolutely untarnished, and has shown no tendency to wet the walls of the pump. A single bubble of ozonised oxygen would, as is well known, cause the mercury to adhere to the glass, and render the pump useless until cleaned. It may therefore be taken as certain that ozone is not produced by the action of radium bromide on water, in absence of organic matter. I have no experiments to show whether the presence of organic matter might not lead to its formation.

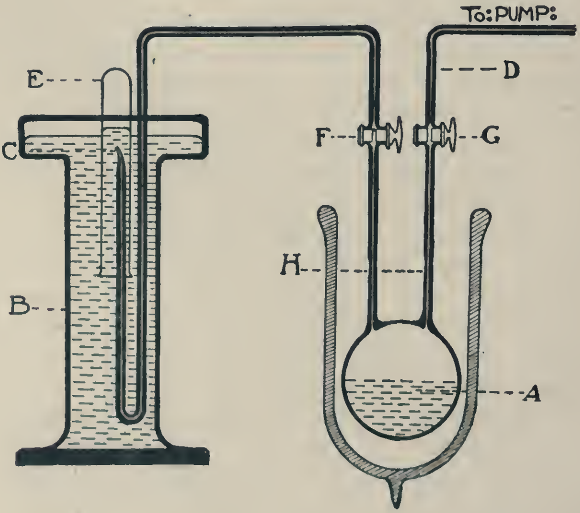
Yet another two suggestions may be made. They are that the radium bromide may be oxidised to bromate, or that hydrogen dioxide may be formed. To test this, I added a drop of a mixture of iodide of potassium and starch, slightly acidified, to an old solution of radium bromide; no coloration was visible. These hypotheses must also be rejected.

3. *The Action of Radium Emanation on Water.*—As already mentioned, the amount of energy evolved during the spontaneous transformation of radium emanation is enormous. Supposing the density of the emanation to be 108, 1 milligram liberates no less than 720,000 gram-calories in thirty days. Supposing, too, that all this energy were expended in decomposing water, it should be sufficient to resolve nearly 200 grams of water into oxygen and hydrogen.

Looking at the question somewhat differently, one cubic millimetre of emanation should liberate about 2·3 litres of explosive gas, if all energy were to be expended in that manner. But although the emanation does decompose water, the amount of water decomposed is far from the quantity mentioned.

The experiments were carried out in the following manner. The bulb *A* (Fig. 1) contained three or four cubic centimetres of pure distilled water. The inverted siphon, *B*, dipping under mercury in the reservoir, was sealed at *C* in such a way that the least pressure broke off its capillary point. The water was then frozen with liquid air, and a vacuum was made through *D*, which was sealed to a Töpler pump. The stop-cocks were then closed, and the emanation drawn from the dissolved radium bromide, and mixed with oxygen and hydrogen, contained in the small gas-tube, *E*, was introduced after explosion into the bulb by pressing the tube down on the point *C*. The gas entered the capillary tube up to the closed stop-cock, *F*. This stop-cock was then cautiously opened, and all gas entered the cooled bulb, care being taken not to introduce any mercury. After some minutes, all emanation had condensed, and the stop-cock, *g*, was opened, and the excess gas, consisting chiefly of hydrogen, was pumped off. Operating in this manner, the bulb contained only water and emanation. The gas removed before sealing the capillaries at *H* was analysed.

FIG. 1.



To ensure complete contact between water and emanation, the bulb was attached to the crank of a small hot-air engine, and shaken continuously for a month.

The results of three experiments are given in the following table:

Initial volume of gas from radium bromide in c.c.	Excess of hydrogen in c.c.	Per cent.	Volume of gas produced by the action of the emanation of water.	Excess of hydrogen.	Per cent.
1. 9·036 *	0·339	3·76	1·810	0·053	2·93
2. 4·765	0·138	2·90	3·561	0·137	3·85
3. 15·590	0·316	2·02	4·023	0·582	14·50

* The volume of the emanation added was of the order of 0·03 cubic millimetres.

I cannot explain the third result; there was no oxidisable matter in the bulb, and the experiment was well carried out.

It is evident that the emanation alone can decompose water, and that it yields excess of hydrogen. The cause of this excess cannot be any one of the possible ones already considered, except the formation of hydrogen peroxide, but even that is excluded by this experiment: the bulb containing the water, after gas had been pumped off, was left in connexion with a tube filled with phosphoric anhydride until all the water had evaporated and had been absorbed by the anhydride. A minute bubble of gas was collected; on explosion, it gave absolutely no residue. Had the water contained peroxide, this bubble should have consisted of oxygen. In the other two experiments the water was tested by means of iodide of potassium and starch; there was no liberation of iodine.*

4. *The Action of the Radium Emanation on a Mixture of Oxygen and Hydrogen.*—An experiment was next made to ascertain whether the presence of the emanation would cause combination of oxygen and hydrogen; the gas extracted from the radium bromide was suitable for this purpose. Some of this mixture was divided into two. The first portion, 3·174 c.c., was exploded; it gave 0·179 c.c. of hydrogen in excess, or 5·64 per cent. The second portion was sealed into a bulb on January 29th, 1905; it was opened on February 20th. It consisted originally of 2·120 c.c., and its final volume was 1·483 c.c.,

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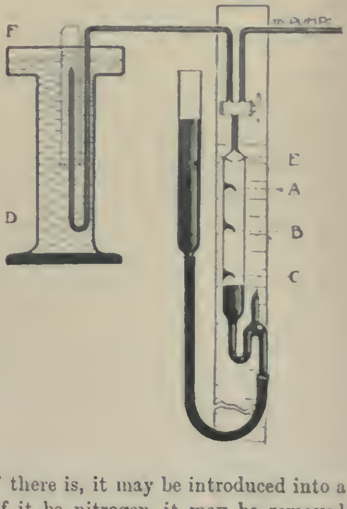
* The method of measuring accurately such minute quantities of gas has been shortly described in the *Proceedings of the Royal Society* for 1905 (**76**, *A*), p. 113. As it may prove useful to chemists, however, a short description, with a drawing, is here appended. A gas-burette, as in the figure, is used. The volumes to the points *A*, *B*, and *C* are accurately known; the gas is introduced through the inverted siphon, *D*; the pressure is measured after the volume has been carefully adjusted to one of the black points; sparks from the terminals at *E* are passed to explode the gas, and it is again measured; pure oxygen, made from permanganate, is then introduced, and it is again measured, exploded, and measured again. The gas is then expelled into the small tube, *F*, into which a little globule of phosphorus has been previously introduced and melted; the top of the tube is gently heated; the phosphorus burns and absorbs oxygen, and the residual gas, if any, is withdrawn and measured; there is usually no residue. If there is, it may be introduced into a spectrum tube and its nature determined; or if it be nitrogen, it may be removed by sparking with oxygen.



equivalent to a recombination of 30 per cent. of the original gas. On explosion, a residue of hydrogen was obtained, equal to 5 per cent. of the original volume, 2·120 c.c.

A second experiment, in which 2·035 c.c. of mixed gases were sealed up with the emanation on November 20th, 1906, the bulb was opened on December 27th, and its volume was then 1·480 c.c., equivalent to a recombination of 27·2 per cent. of the original gas; it contained 5·61 per cent. of excess hydrogen, reckoned on the volume 2·035.

It appears, then, that oxygen and hydrogen recombine in presence of the emanation. The gases were dry when introduced into the bulb, and they were at a reduced pressure, probably about a quarter of an atmosphere, while exposed to the emanation. It may here be mentioned that Messrs. Berger Davis and C. W. Edwards (*J. Soc. Chem. Ind.*, 1905, **24**, 266) noticed that solid radium bromide, left in contact with a mixture of oxygen and hydrogen, induces slow combination.

These experiments prove that the action of the emanation on a mixture of oxygen and hydrogen is a reversible reaction, and that the velocity of decomposition of water is greater than that of recombination of the resulting gases, for water is decomposed by emanation.

5. *The Rate at which Water is Decomposed by Emanation.*—It is difficult to solve this problem, on account of disturbing factors. These are: (1) At the beginning of the experiments the emanation is wholly dissolved in the water. After some hours, gas is evolved, and the emanation divides itself between the water and the gaseous mixture, in such a manner that that part of the emanation which remains in solution decomposes the water, and it is to be presumed that the portion mixed with the gases causes them to recombine. An experiment has not been made (and it would be very difficult to carry out) to test whether steam is decomposed by the emanation. (2) It was impossible to prevent the gaseous mixture touching the stopcock, and consequently coming into contact with grease; when this occurs, carbon monoxide and dioxide are produced. (3) It was impracticable to avoid the use of mercury, and it has been mentioned that mercury is oxidised. But below the fairly deep layer of water the mercury, it should be noted, remained untarnished. Hence the results do not show correspondence between the amount of emanation present and its quantitative action on water. Moreover, it is not improbable that some of the products of the change of the emanation have also an action in decomposing water, although nothing is known as regards this. In spite of these objections, the results are perhaps worth recording.

The initial gas was obtained from 212 milligrams of radium bromide in three days; its volume at normal temperature and pressure was

3·935 c.c. After explosion, the excess of hydrogen was removed by addition of a sufficient quantity of oxygen; the final residue, amounting to 0·093 c.c., was introduced over several cubic centimetres of water, standing over mercury in a measuring-tube provided with a black point, to which the level of the water could be adjusted. The minute bubble was well shaken with the water, and allowed to stand from November 25th, 1905, until January 8th, 1906; and daily readings were taken, temperature and pressure being noted, and the pressure of water-vapour allowed for. The readings are as follows:

	0.	1.	2.	3.	4.	5.	
November	25.	26.	27.	28.	29.	30.	
C.c.	0·093	0·611	0·980	1·23	1·42	1·57	
	6.	7.	8.	9.	10.	11.	12.
December.........	1.	2.	3.	4.	5.	6.	8
C.c.	1·66	1·74	1·79	1·84	1·88	1·94	1·98
	13.	14.	15.	16.	17.		18.
December.........	9.	10.	11.	12.	13.	Jan.	8.
C.c.	2·07	2·00	2·00	2·01	2·04		2·14

This final gas was then analysed.

Assuming that the initial gas present was oxygen, its composition was:

Oxygen originally present...	0·093 c.c.	
Carbon dioxide	0·850 ,,	
Hydrogen and oxygen	0·726 ,,	
Excess hydrogen	0·471 ,,	equivalent to 23·0 per cent.
	2·140 c.c.	

It would be natural to suppose that if all emanation remained dissolved, not escaping into the gases produced, the rate of decomposition of the water would be proportional to the rate of decay of the emanation, supposing the decomposition of the emanation to be due solely to the latter; if, however, the decay of other products, radium *A*, radium *B*, and radium *C*, is also accompanied by the decomposition of water, the problem becomes a very complicated one..

The curve obtained by plotting the rate of increase of the gases formed against time shows a much more rapid increase than the rate of decay of the emanation would warrant. The period of half-value of the emanation is 3·8 days, that of the increase of gases is 2·53 days. The curves, however, resemble each other in character. The lives of radium *A*, radium *B*, and radium *C* are very short, their combined half-period of decay being less than an hour; but as they are being continuously produced, owing to the decay of the emanation, a constant maximum is quickly produced, which falls off as the emanation decays. Attempts to allow for this disturbing influence have been made, but without success, and it appears probable that the partition of the emanation between gas and water, and the recombination of the hydrogen and oxygen in the gaseous system, render any such attempts futile in the present state of our knowledge.

I wish to take this opportunity of thanking Mr. Alfred Porter and Mr. Cameron for their help in attempting the mathematical analysis of these phenomena.

LXXXVII.—*The Chemical Changes induced in Gases submitted to the Action of Ultraviolet Light.*

By David Leonard Chapman, Samuel Chadwick, and John Edwin Ramsbottom.

The investigation which forms the subject of the present paper was suggested by the work of Burgess and Chapman on the interaction of chlorine and hydrogen, and it was started shortly after the inhibitive effect of compounds of ammonia on the above reaction was discovered. The circumstance that traces of such impurities completely prevented the interaction of chlorine and hydrogen submitted to the action of light could in the opinion of Burgess and Chapman be best explained on the supposition that the inhibitor altered the character of the vibrations set up by the light in the various species of molecules of which the system was composed; that, in fact, the presence of a trace of a suitable catalyst so materially altered the whole mode of degradation of the highly efficient light energy that the relative number of pairs of chlorine and hydrogen molecules in such states of vibration as to be capable of interacting was very considerably reduced.*

Now there is no reason why the accelerating effect of a positive catalyst such as moisture should not be ascribed to a similar cause, and therefore the present authors determined to search for evidence for or against this view. The typical example of a reaction influenced by moisture, namely, the interaction of carbon monoxide and oxygen (Dixon, *Brit. Assoc. Report*, 1880, 503) was selected as being for several reasons the most suitable for investigation. Some means had

* The results of a recent investigation on the retardation of the rate of combination of chlorine and hydrogen by oxygen (which it is hoped to publish shortly) lend some support to this view concerning the cause of inhibition by impurities.

to be found whereby these two gases could be caused to interact slowly out of the presence of any other catalyst except moisture. The only possible method of accomplishing this object was by the gases being subjected to the influence of some form of radiant energy such as the cathode rays, ultraviolet light, or the silent or disruptive electric discharge.* Of these ultraviolet light was to be preferred because of the complexity of the electric discharge and of the circumstance that the cathode rays in their passage through gases give rise to other forms of energy. A few cases in which the cathode rays and ultraviolet light induce chemical changes had been discovered already.

Ph. Lenard (*Ann. Physik.*, 1894, 51, 225) had shown that cathode rays which had penetrated an aluminium window in a vacuum tube produced ozone in the air through which they passed. Whether the formation of ozone was due directly to the cathode rays or indirectly to the ultraviolet light produced by the passage of the cathode rays through air is doubtful. Lenard was unable to detect any other chemical changes induced by the action of this form of energy; electrolytic gas did not explode, carbon disulphide did not burn, hydrogen sulphide was unchanged, and nitrogen and hydrogen did not combine in the presence of the rays.

Lenard (*Ann. Physik.*, 1900, 70, 486) also investigated somewhat exhaustively the effects of ultraviolet light on gases. He showed, firstly, that under the influence of light gases became conducting; secondly, that condensation nuclei were produced, and, thirdly, that in the case of oxygen ozone was formed. These effects were brought about in air by light of wave-length 0·00014 mm. to 0·00019 mm., that is, only by the rays of highest refrangibility to which air is comparatively opaque. Hydrogen was more transparent to ultraviolet light than air, and was accordingly unaffected by light of greater wave-length than 0·00016 mm. To the most chemically active rays, air at atmospheric pressure was more opaque than rock salt, fluorspar, or quartz. It is important that this relative opacity of air should be borne in mind in the construction of any apparatus to be used in the examination of the chemical effects of rays, and that air-spaces in the path of the rays should be avoided.

Closely connected with the subject is an interesting research by E. Warburg (*Sitzungsber. K. Akad. Wiss., Berlin*, 1903, 1011), in which the discharge of electricity through oxygen from a point was investigated. Under different conditions the amount of ozone produced was from 1000 to 93 times greater than the amount which would have been found had its production been due entirely to electrolysis. From this fact the necessary conclusion was drawn that ozone produced in the path of the electric discharge results from the action of ultraviolet light and cathode rays on oxygen, a view which received further support from the circumstance that the amount of ozone formed in a given time was roughly proportional to the intensity of the light.

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* There are various reasons for thinking that the chemical effects brought about by the electric discharge are mainly due either to the cathode rays or to ultraviolet light, or to both combined.

E. Warburg and E. Regener (*Sitzungsber. K. Akad. Wiss., Berlin*, 1904, 1228) were the first to demonstrate that ultraviolet light could induce other chemical changes besides the conversion of oxygen into ozone. As a source of ultraviolet light they employed an electric spark between aluminium electrodes. With their apparatus 2·2 * per cent. of oxygen at atmospheric pressure could be converted into ozone. They found that ammonia, nitric oxide, and nitrous oxide were readily decomposed by the light.

As a source of ultraviolet light we have used a quartz mercury lamp, the light from which has been shown by A. Pfluger (*Physikal. Zeitsch.*, 1904, 5, 414) and Ladenburg (*Physikal. Zeitsch.*, 1904, 5, 525) to be rich in ultraviolet rays. The formation of ozone from oxygen submitted to the action of the light from a quartz mercury lamp specially constructed for the purpose has been investigated already by Franz Fischer and Fritz Braehmer (*Ber.*, 1905, 38, 2633). The maximum percentage of oxygen converted into ozone when a current of the gas was passed through the apparatus was only 0·26. Their primary object, however, was not to obtain a large percentage of ozone, but to estimate the yield for a given expenditure of energy under various conditions. For our purpose, the apparatus used by Fischer and Braehmer would have been unsuitable, particularly as the gases under investigation came into contact with an organic cement. Impurities in the gases would have rendered our results valueless.

The gases to be acted on were enclosed in a bulb of fused quartz through which ultraviolet light was caused to pass from the outside. Ultraviolet light partly owes its exceptional photochemical efficiency to the circumstance that it is absorbed with relative ease by most substances, including the colourless gases; but this characteristic is also the cause of most of the difficulties which arise in an experimental investigation of the effects produced by it. To obtain the best results the apparatus should, as a general rule, be constructed so that the light has to pass only through a vacuum or vitreous quartz. As the wave-length of the effective light decreases, the necessity of observing this precaution becomes greater. At first an iron arc placed at a few centimetres from the quartz vessel which contained the gases to be acted on was used, but the chemical effects induced by the light capable of penetrating the layer of intervening air were too small to be accurately measured. Then the quartz vessel was illuminated by the rays from a mercury arc, the arc being in the same evacuated space as the quartz vessel, but at a short distance from it. This arrangement was also ineffective, owing no doubt to the most chemically active rays having been absorbed by the layer of non-luminous mercury vapour surrounding the arc. Finally, the quartz bulb was placed within the mercury arc, proper precautions being taken to prevent the temperature of the gases contained in it from rising more than a few degrees. The accompanying figure is a diagram of the apparatus in its final form.

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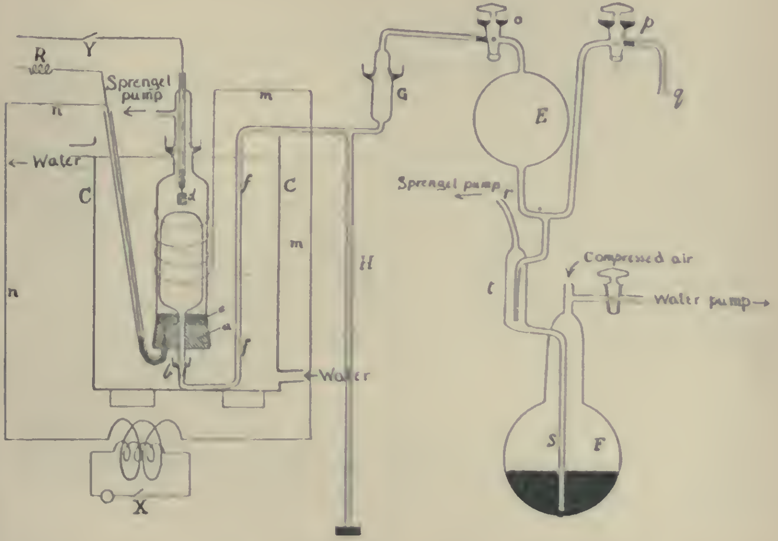
* The low percentage of ozone was attributed to the property which some of the rays were supposed to possess of destroying the ozone formed.



The gases which we desired to submit to the action of ultraviolet light were contained within the cylindrical quartz vessel, *A*. This vessel was enclosed within a glass mercury lamp, *B*, of which the cathode was a pool of mercury, *e*, and the anode, a short cylinder of iron, *d*. Whenever the current passed between *e* and *d* the quartz vessel was completely surrounded with the arc, and the light had only to pass through 1½ mm. of vitreous quartz to reach the gas contained within it. The distance between the inner surface of the mercury lamp and the outer surface of the quartz cylinder was 2 mm. The mercury lamp was exhausted with a Sprengel pump. The method of making electrical connexion with the electrodes *e* and *d* can be seen from the figure. The neck of the quartz vessel, *A*, after passing through the stopper, *a*, which closed the lower end of the mercury lamp, was connected with the tube, *f*, by means of the ground-glass mercury joint, *b*. The mercury lamp was contained in a bath, *C*, through which a rapid current of cold water was caused to flow continuously. The bath was supported on blocks of paraffin wax.

As it was desirable that the temperature of the quartz vessel should not rise more than a few degrees, the electric current was passed through the mercury lamp for one second only at the end of every half minute, the heat developed in the arc during one second being thus allowed half a minute to escape. It was estimated that in an experiment conducted on this plan no portion of the gas under examination ever acquired a temperature of more than 40°. That part of the apparatus by which the arc was struck every half minute and maintained in action for one second only is represented in the figure diagrammatically. The terminals of the secondary coil of an induction coil were connected with the outside of the lamp, *B*, and the mercury electrode, *e*, by the fine wires *m* and *n* respectively. The current through the primary coil of the induction coil could be made and broken by the contact breaker, *X*. A current of 6 amperes regulated by means of a resistance, *R*, was supplied to the mercury lamp. A mercury contact breaker, *Y*, served to close the circuit. When *X* was closed a high tension discharge filled the mercury lamp, and this was sufficient to strike the arc on *Y* being closed. It was arranged that *X* and *Y* should remain closed for one second, but that the closing of *X* should take place a fraction of a second before that of *Y*, the apparatus being so adjusted that the above sequence of events should recur every half minute.

The currents were made and broken by a contrivance, not shown in the figure, which was regulated electrically by a clock. The other details connected with this part of the apparatus do not require description.

At *q* was a ground glass mercury joint by means of which connexion could be made with any apparatus intended for the preparation of one or other of the gases required in an experiment. Through the tube *r* gas could be withdrawn by a Sprengel mercury pump. The taps *o* and *p* were not lubricated and accordingly were not completely airtight. The tube on either side of each tap could, however, be sealed when necessary with mercury as shown in the figure, the prevention of the escape of gas in one direction (which was all that was required) being thereby achieved. The flask *F* contained mercury which could be raised by way of the tube *S* and trap *t* as far as the taps *o* and *p* by the forcing of air into the flask with a pump. By *F* being brought into communication with a water pump the mercury could be lowered again. The customary device of a movable mercury reservoir joined to the apparatus by a rubber tube was not resorted to because mercury in flowing through a rubber tube always carries with it a small amount of organic impurity. The tube *G* was introduced for the purpose of containing phosphoric oxide. The gas was passed backwards and forwards many times through the phosphoric oxide and was thereby dried, the mercury in globe *E* being raised and lowered alternately for the purpose.

The oxygen used in the experiments was prepared by heating potassium permanganate; the carbon monoxide by the action of a mixture of equal volumes of sulphuric acid and water on sodium formate, the gas being washed with potash solution; and the carbon dioxide by the action of dilute sulphuric acid on sodium bicarbonate.

Conversion of Oxygen into Ozone.

The experiments on the conversion of oxygen into ozone were performed mainly for the purpose of testing the efficiency of the apparatus. It was found that a mercury manometer could be used to estimate the pressure provided that the manometer was connected with the quartz vessel by a sufficient length of capillary glass tubing. The oxygen was imperfectly dried, having been passed only once through the tube *G* containing phosphoric oxide. The temperature of the bath varied between 8° and 9°. As was to be expected, the rate of formation of ozone was comparatively rapid at first, but fell continuously until after the lapse of five hours—that is, after the oxygen had been exposed for ten minutes in all to the light of the lamp—equilibrium had almost been attained. 3·5 per cent. of oxygen had been converted into ozone. This is the largest percentage of ozone yet obtained by any means other than the silent discharge.

Interaction of Carbon Monoxide and Oxygen.

In these experiments oxygen in excess of that required to convert the carbon monoxide into carbon dioxide was taken, since it was anticipated that with such a mixture the relative rates of formation of ozone and of carbon dioxide could be more accurately studied.

Experiment I.—Carbon monoxide and oxygen, dried by being passed through strong sulphuric acid, were present in equal volumes. When the mixed gases had been exposed for six hours to the intermittent light, that is, to the light of the lamp for twelve minutes, the contraction was 15·54 per cent. of the total volume. After the experiment a sample of gas was withdrawn and the ratio of carbon monoxide to carbon dioxide contained in it was determined by analysis. The ratio of carbon monoxide to oxygen in the original mixture had previously been found. These two ratios together with the percentage contraction are sufficient data for calculating the composition of the final mixture.

The actual values found for the two ratios were:

$\frac{CO_2}{CO}$ in the gases which had been submitted to the action of the light $= 0{\cdot}2979$.

$\frac{O_2}{CO}$ in the original mixture $= 0{\cdot}949$.

Whence the compositions of the original and final mixtures are found to be:

Original Mixture.	*Final Mixture.*
$O_2 = 48{\cdot}69$ volumes	$O_3 = 19{\cdot}30$ volumes
$CO = 51{\cdot}31$,,	$CO_2 = 11{\cdot}78$,,
	$CO = 39{\cdot}53$,,
100 ,,	$O_2 = 13{\cdot}85$,,
	84·46 ,,

Now carbon monoxide is not appreciably affected by ultraviolet light, whereas oxygen is readily converted into ozone, so that it would appear reasonable to assume that the first chemical effect of the ultraviolet light is the decomposition of the oxygen molecules into atoms, and then the immediate combination of the latter either with oxygen molecules or with carbon monoxide molecules according to the equations:

$$O_2 = O + O$$
$$O_2 + O = O_3$$
$$CO + O = CO_2$$

These equations are not necessarily a complete expression of the truth, but they would appear to be the simplest representation of the facts known at present, so far, at any rate, as these facts can be represented by equations at all. It is conceivable, for example, that ozone and carbon dioxide might be formed without actual dissociation of the oxygen molecules being inevitably involved, but in this event the argument which follows would not be invalidated. The high percentage of ozone in comparison with that of carbon dioxide in the final mixture is significant, and points to the conclusion that the tendency of an atom of oxygen to combine with a molecule of oxygen must be somewhat greater than that of an atom of oxygen to combine with a molecule of carbon monoxide when the gases are dry.

The stability of the ozone formed under the conditions of the experiment is also remarkable and affords material for future speculation and research. Is ozone more stable in all circumstances in the presence of oxides of carbon, or do the oxides of carbon inhibit the decomposition of ozone by the deozonising rays assumed by Warburg to be present in ultraviolet light? This problem is one which we hope at an early date to attack.

Experiment II.—This experiment was a repetition of the last, with one variation. The gases were dried with greater care, the desiccating agent being pure redistilled phosphoric oxide. The gases were submitted to the intermittent light for eight hours, and therefore the time during which they were exposed to the light of the lamp was in all sixteen minutes. The following results were obtained:

Contraction = 14·13 per cent. of original volume.

$\frac{\mathrm{CO}_2}{\mathrm{CO}}$ in the gases which had been submitted to the light = 0·2419.

$\frac{\mathrm{O}_2}{\mathrm{CO}}$ in the original mixture = 1·015.

Whence we deduce:

Original Mixture.	*Final Mixture.*
O_2 = 50·38 volumes	O_3 = 18·59 volumes
CO = 49·62 „	CO_2 = 9·67 „
	CO = 39·95 „
100 „	O_2 = 17·66 „
Contraction = 100 − 85·87 volumes.	85·87 „

A comparison of the results of the first experiment with those obtained in the one just quoted discloses the fact that the trace of moisture left after drying with sulphuric acid is only capable of raising the value of the ratio $\frac{\mathrm{CO}_2}{\mathrm{O}_3}$ above that of the carefully dried gases by a small amount. The effect of a further increase in the percentage of moisture on the ratio in question is, however, very considerable, as the following experiment demonstrates.

Experiment III.—A mixture of approximately equal volumes of carbon monoxide and oxygen, saturated with water vapour at 16°, was submitted to the action of the intermittent light for ten hours. The rate of contraction was a little slower than in the two preceding experiments. The analysis of the resulting mixture showed that the contraction was in this case almost entirely due to the formation of carbon dioxide. The composition of the final mixture was as under:

O_3.	CO_2.	CO.	O_2.	Contraction.
1·31	27·90	21·72	35·12	13·95 volumes

On repeating this experiment we obtained a similar result.

One interesting fact is clearly brought to light by a comparison of the results of the three experiments. The rate of chemical change as measured by the contraction was practically the same in every case, for although the presence of moisture resulted in an increase in the amount of carbon dioxide formed in a given time, it reduced the yield of ozone by an equivalent amount. A simple explanation is afforded by the hypothesis that the dissociation of diatomic oxygen proceeds with equal facility in the absence and presence of moisture, and that the oxygen atoms resulting from the dissociation immediately enter into combination either with oxygen or with carbon monoxide molecules, the chances of a union taking place with the latter class of molecules being greater in the presence of moisture. It is conceivable that the moisture might increase the chances of combination of carbon monoxide molecules with oxygen atoms in two possible ways, but to which of these preference should be given in the case under discussion is not at present clear.

In the first place, the reaction represented by the equation

$$CO + O \longrightarrow CO_2$$

is accompanied by change of potential energy into highly efficient kinetic energy. The absence of any means by which this kinetic energy might be degraded into a less efficient form would simply result in its reconversion into potential energy, that is, the reaction would not take place. So that if water could aid the kinetic energy to degrade into heat it would be able to accelerate the chemical change in question.

In the second place, for two substances to interact the molecules of each must first be brought into a suitable state of vibration, and the addition of a third substance, such as moisture, to the system might result in a change of distribution of the vibrational energy, the pairs of molecules in a state of vibration conducive to interaction being either increased or decreased in number thereby.

The conjecture that the distribution of energy is essentially different in two mixtures of carbon dioxide, carbon monoxide, and oxygen of the same composition, except in respect of their content of moisture, and illuminated by light of the same intensity, receives confirmation from the experimental results quoted below.

Experiments on the Decomposition of Carbon Dioxide by Ultraviolet Light.

The method of working has already been sufficiently indicated; a description, therefore, of most of the details of these experiments can be omitted.

*Experiments at Atmospheric Pressure.**—It was found that after long exposure to the intermittent light, dry carbon dioxide at atmospheric pressure was decomposed to an extent from 2·6 to 3 per cent. The amount of decomposition was in each case estimated by the ratio of carbon monoxide to carbon dioxide in the resulting gases. The oxygen was partially ozonised.

When the moist carbon dioxide was submitted to the action of ultraviolet light, no increase of pressure within the apparatus could be observed, and no carbon dioxide could be detected in the gases withdrawn after the experiment.

Experiments at Reduced Pressure.—Carbon dioxide nearly saturated with water vapour was admitted to the apparatus until the pressure was equal to that of the atmosphere. Gas was then withdrawn until the manometer indicated that the pressure within the apparatus was 30 mm. The pressure did not increase when the gas was submitted to the action of ultraviolet light, and the gas withdrawn at the end of the experiment did not contain either carbon monoxide or oxygen. When the alkaline pyrogallol was added, a slight change in its colour was noted, but no decrease in the volume of the gas could be detected.

Carefully dried carbon dioxide at a pressure of 36 mm. was next submitted to the action of the intermittent light for forty-five hours. The analysis of the gases withdrawn at the end of the experiment showed that 46 per cent. of the carbon dioxide had been decomposed.

The above experiments demonstrate that dry carbon dioxide is decomposed by ultraviolet light, the percentage decomposition being increased by a reduction of pressure, but that under the same conditions the moist gas at all pressures remains practically unchanged. Now it is well known that in a balanced reaction in a system kept at the same temperature as its surroundings the state of equilibrium is unaffected by a small amount of a catalyst. The extent, for example, to which carbon dioxide is decomposed when it is maintained at constant temperature in an opaque vessel is dependent only on the temperature and pressure, and is independent of the degree of desiccation. The reason for this well-established fact is that the distribution of energy amongst the various groups of molecules after equilibrium has been established is unaffected by the presence of a small amount of a foreign substance.

When, on the other hand, the reaction is photochemical, the position of equilibrium is not independent of the catalyst, as the above experiments demonstrate, and this fact impels us to conclude that under such conditions the catalyst (moisture) exerts a marked influence in determining the mode of distribution of the energy amongst the molecules of the reacting substances (the two oxides of carbon and oxygen). The experiments on the decomposition of moist and dry carbon dioxide therefore appear to afford a simple means of demonstrating the truth of one of our principal assumptions.

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* H. Buff and A. W. Hofmann (Trans., 1860, **12**, 282) decomposed carbon dioxide at atmospheric pressure by electric sparks. H. B. Dixon and Lowe (Trans., 1885, **47**, 571) showed that dry carbon dioxide is decomposed by sparks between metal electrodes to an extent of from 20 to 43 per cent.

THE UNIVERSITY OF MANCHESTER.

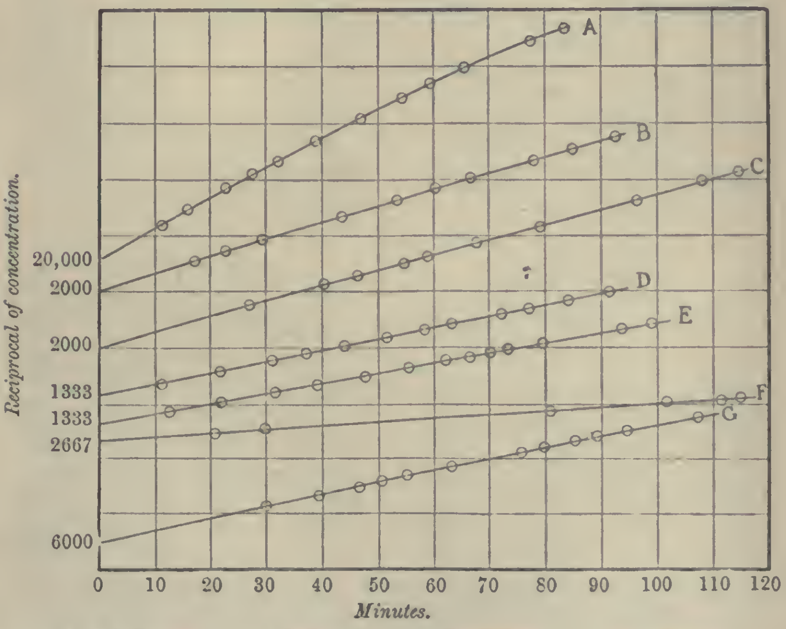
LXXXVIII.—*The Velocity of Hydrolysis of the Aliphatic Amides by Alkali.*

By JAMES CODRINGTON CROCKER, M.A., D.Sc., and FRANK HAROLD LOWE, M.Sc.

IN continuation of the work by one of the authors (this vol., 593) the velocities of hydrolysis of the aliphatic amides by alkali have been investigated. It was thought that the work might throw some light on the question as to whether any essential difference exists between the reactions of hydrolysis by acid and by alkali.

The results of Arrhenius (*Zeitsch. physikal. Chem.*, 1899, **28**, 329) in the case of ethyl acetate appear to show that there is a difference in the mechanism of the reactions. The temperature-coefficients of reactivity are very different for the two cases. On the other hand, in the cases of the action of water on chloroacetic acid, and alkali on sodium chloroacetate, quoted by Arrhenius (*Zeitsch. physikal. Chem.*, 1889, **4**, 226), the temperature-coefficients of reactivity are nearly equal, which would appear to indicate that the mechanism of the reactions is the same in both cases, and that the action of alkali is to be here regarded as catalytic. The experiments in the present work were conducted at three temperatures, 40·06°, 63·2°, and 95·9°. The apparatus used and the method of experiment were the same as previously described. The aqueous solution of the amide was in each case hydrolysed by an equivalent aqueous solution of caustic soda in the conductivity cell. For the purpose of standardising the original conductivity-time curves and deducing the concentration-time relations, synthetical mixtures of amide, caustic soda, sodium acetate, and ammonia were made up generally representing the conditions at 0, 25, 50, and 100 per cent. of the reaction. From the rate of change of conductivity, the initial conductivity in each case was deduced by extrapolation of the resistance-time curve. The values for the velocity constants were calculated from the formula $K = \frac{1}{at}\left(\frac{1}{c} - \frac{1}{c^0}\right)$, where a is the degree of dissociation of the caustic soda. These values were obtained by plotting the degree of dissociation taken from the results of Arrhenius (*Zeitsch. physikal. Chem.*, 1889, **4**, 99) with temperature. Satisfactory agreement with the formula given above was obtained in each case and therefore the reactions are all bimolecular. The results were checked by drawing graphs between the reciprocal of concentration and time (see below). If Q is the slope of the curve in c.c. per minute, then $K = Q/a$. It will be seen that these graphs are practically straight lines, with a very slight downward curvature. This is best shown in the case of formamide, where the range of reaction was greatest, and it is evident therefore that the presence of the neutral salt has a slight retarding effect. This also appears from the tables of experimental results.

The graphs for the amides investigated at 40·06° are shown below.



A = Formamide. B = Acetamide. C = Propionamide. D = Butyramide. E = *iso*Butyramide. F = Valeramide. G = Capronamide.

The abscissæ represent, $2t$ for formamide, t for acetamide and propionamide, $t/2$ for butyramide, *iso*butyramide, and capronamide, $t/4$ for valeramide. Each division of the ordinate is equal to 500 c.c., except for formamide, where one division is equal to 5000 c.c.

In the following tables:

t = time in minutes.
σ = specific conductivity of solution in mhos. per c.c.
C = concentration of amide or alkali in gram-equivalents per c.c.
K = velocity-constant.
σ^β = specific conductivity of solution when fraction β of amide is decomposed.

Temperature = 40·06°.

Formamide.

40 c.c. $N/10$-formamide. 40 c.c. $N/10$-NaOH. $Q=280$, $\alpha=0{\cdot}9208$.

t.	$\sigma\times10^3$.	$C\times10^6$.	K.
23·00	11·98	37·65	313·5
27·75	11·67	35·75	311·9
30·00	11·55	35·00	310·2
32·33	11·42	34·30	307·3
34·92	11·31	33·62	303·0
37·16	11·18	32·85	305·1
39·00	11·10	32·35	303·8
40·66	11·04	32·00	300·4

Mean $K=306{\cdot}9$

$\sigma^0=0{\cdot}01409$, $\sigma^{0\cdot25}=0{\cdot}01188$.
$\sigma^{0\cdot5}=0{\cdot}00991$, $\sigma^1=0{\cdot}00643$.

K calculated from slope of curve = 304·1.

Acetamide.

20 c.c. N-acetamide. 20 c.c. N-NaOH. $Q=7{\cdot}540$. $\alpha=0{\cdot}8351$.

t.	$\sigma\times10^2$.	$C\times10^5$.	K.
34·58	10·86	40·18	9·143
87·16	9·743	37·50	9·162
107·16	9·412	35·62	9·016
120·75	9·202	34·30	9·074
133·90	9·026	33·25	9·010
169·58	8·582	30·58	8·962
185·30	8·410	29·57	8·930
217·75	8·042	27·40	9·072

Mean $K=9{\cdot}046$

$\sigma^0=0{\cdot}1185$, $\sigma^{0\cdot25}=0{\cdot}09743$,
$\sigma^{0\cdot5}=0{\cdot}07626$, $\sigma^1=0{\cdot}04046$.

K calculated from slope of curve = 9·031.

Propionamide.

40 c.c. $N/10$-propionamide. 40 c.c. N-NaOH. $Q=6{\cdot}871$. $\alpha=0{\cdot}8351$.

t.	$\sigma\times10^2$.	$C\times10^5$.	K.
80·42	9·743	39·05	8·352
97·75	9·464	37·50	8·170
109·42	9·279	36·40	8·204
135·83	8·906	34·20	8·145
158·08	8·628	32·60	8·079
229·60	7·852	28·00	8·191
263·08	7·582	26·40	8·137
312·4	7·251	24·36	8·141

Mean $K=8{\cdot}177$

$\sigma^0=0{\cdot}1163$, $\sigma^{0\cdot25}=0{\cdot}09462$,
$\sigma^{0\cdot5}=0{\cdot}07375$, $\sigma^1=0{\cdot}03747$.

K calculated from slope of curve = 8·221.

Butyramide.

20 c.c. $1\frac{1}{2}N$-butyramide. 20 c.c. $1\frac{1}{2}N$-NaOH. $Q=2{\cdot}458$. $\alpha=0{\cdot}8194$.

t.	$\sigma\times10^2$.	$C\times10^5$.	K.
149·3	12·76	58·80	3·007
199·6	12·16	54·80	3·007
233·2	11·81	52·43	3·004
253·3	11·61	51·11	3·007
289·2	11·29	48·90	3·004
308·3	11·13	47·82	3·000
322·3	11·01	47·00	3·010
336·3	10·90	46·30	3·001

Mean $K=3{\cdot}005$

$\sigma^0=0{\cdot}1538$, $\sigma^{0\cdot25}=0{\cdot}1239$,
$\sigma^{0\cdot5}=0{\cdot}09625$, $\sigma^1=0{\cdot}04706$.

K calculated from slope of curve = 3·00.

iso*Butyramide.*

20 c.c. $3N/2$-*iso*butyramide. 20 c.c. $3N/2$-NaOH. $Q=2{\cdot}186$. $\alpha=0{\cdot}8194$.

t.	$\sigma\times10^2$.	$C\times10^5$.	K.
51·00	14·45	69·30	2·632
75·67	14·05	66·80	2·644
109·66	13·56	63·70	2·637
127·25	13·31	62·10	2·655
142·08	13·13	60·90	2·655
221·40	12·20	54·90	2·689
294·00	11·54	50·50	2·686
335·16	11·21	48·30	2·684

Mean $K=2{\cdot}660$

$\sigma^0=0{\cdot}1541$, $\sigma^{0\cdot25}=0{\cdot}1240$,
$\sigma^{0\cdot5}=0{\cdot}09634$, $\sigma^1=0{\cdot}04785$.

K calculated from slope of curve $=2{\cdot}668$.

Valeramide.

20 c.c. $3N/4$-valeramide. 20 c.c. $3N/4$-NaOH. $Q=0{\cdot}4145$. $\alpha=0{\cdot}8461$.

t.	$\sigma\times10^3$.	$C\times10^5$.	K.
200	86·36	36·25	0·5376
650	82·41	34·14	0·4782
675	82·06	34·00	0·4797
720	81·28	33·55	0·5153
785	81·14	33·42	0·4983
813	80·78	33·21	0·5000
870	80·30	32·95	0·4998
1005	79·49	32·55	0·4763

Mean $K=0{\cdot}4981$

$\sigma^0=0{\cdot}08859$, $\sigma^{0\cdot25}=0{\cdot}07178$,
$\sigma^{0\cdot5}=0{\cdot}05567$, $\sigma^1=0{\cdot}02762$.

K calculated from slope of curve $=0{\cdot}4892$.

Capronamide.

20 c.c. $N/3$-capronamide. 20 c.c. $N/3$-NaOH. $Q=2{\cdot}700$. $\alpha=0{\cdot}8750$.

t.	$\sigma\times10^3$.	$C\times10^5$.	K.
138·5	39·93	15·69	3·069
186·0	39·38	15·39	3·060
253·0	38·59	14·96	3·080
279·5	38·33	14·81	3·075
303·2	38·06	14·67	3·076
341·0	37·67	14·45	3·083
383·2	37·30	14·25	3·035
428·3	36·86	14·00	3·057

Mean K = 3·067

$\sigma^0=0{\cdot}04167$, $\sigma^{0\cdot25}=0{\cdot}03512$, $\sigma^{0\cdot5}=0{\cdot}02694$, $\sigma^1=0{\cdot}0139$.

K calculated from slope of curve $=3{\cdot}083$.

Temperature = 63·2°.

Formamide.

40 c.c. $N/20$-formamide. 40 c.c. $N/20$-NaOH. $Q=16{\cdot}72$. $\alpha=0{\cdot}9430$.

t.	$\sigma\times10^4$.	$C\times10^6$.	K.
6·16	79·73	19·90	1764
7·21	78·52	19·25	1756
8·70	76·60	18·30	1784
10·58	74·66	17·30	1784
12·66	72·75	16·38	1764
16·38	69·64	14·80	1780
24·50	64·93	12·35	1773
33·00	61·46	10·35	1801

Mean $K=1776$

$\sigma^0=0{\cdot}008936$, $\sigma^{0\cdot225}=0{\cdot}007868$,
$\sigma^{0\cdot475}=0{\cdot}00675$, $\sigma^1=0{\cdot}004715$.

K calculated from slope of curve $=1773$.

Acetamide.

40 c.c. $N/2$-acetamide. 40 c.c. $N/2$-NaOH. $Q=40{\cdot}07$. $\alpha=0{\cdot}8525$.

t.	$\sigma\times10^3$.	$C\times10^5$.	K.
23·23	72·45	22·28	47·00
30·19	70·22	19·18	47·12
36·68	68·40	18·20	47·82
52·55	64·61	16·35	47·28
70·03	60·91	14·70	47·00
87·16	58·46	13·30	47·38
104·71	56·12	12·20	47·02
112·05	55·30	11·80	46·86

Mean $K=47{\cdot}18$

$\sigma^0=0{\cdot}082$, $\sigma^{0\cdot1875}=0{\cdot}07262$,
$\sigma^{0\cdot5625}=0{\cdot}05338$, $\sigma^1=0{\cdot}03263$.

K calculated from slope of curve $=47{\cdot}12$

Propionamide.

40 c.c. *N*/2-propionamide. 40 c.c. *N*/2-NaOH. $Q = 35{\cdot}09$. $\alpha = 0{\cdot}8525$.

t.	$\sigma \times 10^3$.	$C \times 10^5$.	*K.*
13·58	77·13	22·33	41·30
38·68	68·59	18·60	41·10
44·00	67·15	17·97	41·70
64·78	62·52	15·92	41·33
77·50	60·23	14·90	41·02
93·55	57·66	13·73	41·20
103·86	56·25	13·12	40·93
112·33	55·18	12·65	40·81

Mean $K = 41{\cdot}17$

$\sigma^{0} = 0{\cdot}08297$, $\sigma^{0\cdot25} = 0{\cdot}06886$,
$\sigma^{0\cdot5} = 0{\cdot}05484$, $\sigma^{1} = 0{\cdot}03055$.

K calculated from slope of curve = 41·15.

Butyramide.

40 c.c. *N*/2-butyramide. 40 c.c. *N*/2-NaOH. $Q = 14{\cdot}29$. $\alpha = 0{\cdot}8525$.

t.	$\sigma \times 10^3$.	$C \times 10^5$.	*K.*
41·83	74·90	21·77	16·63
58·00	72·49	20·68	16·89
67·33	71·25	20·18	16·65
86·42	68·59	19·03	17·03
110·25	65·90	17·84	17·04
160·50	61·25	15·83	16·92
191·66	59·00	14·80	16·88
246·83	55·44	13·15	17·14

Mean $K = 16{\cdot}89$

$\sigma^{0} = 0{\cdot}0820$, $\sigma^{0\cdot25} = 0{\cdot}06785$,
$\sigma^{0\cdot5} = 0{\cdot}0540$, $\sigma^{1} = 0{\cdot}02916$.

K calculated from slope of curve = 16·76.

iso*Butyramide.*

40 c.c. *N*/2-*iso*butyramide. 40 c.c. *N*/2-NaOH. $Q = 13{\cdot}33$. $\alpha = 0{\cdot}8525$.

t.	$\sigma \times 10^5$.	$C \times 10^5$.	*K.*
31·83	76·95	22·65	15·30
40·92	75·52	22·06	15·34
67·83	71·60	20·35	15·35
102·33	67·62	18·65	15·61
177·92	66·03	17·90	15·79
150·16	63·22	16·67	15·82
180·83	60·80	15·58	15·70
254·50	56·30	13·40	15·96

Mean $K = 15{\cdot}61$

$\sigma^{0} = 0{\cdot}08246$, $\sigma^{0\cdot25} = 0{\cdot}06777$,
$\sigma^{0\cdot5} = 0{\cdot}05419$, $\sigma^{1} = 0{\cdot}02969$.

K calculated from slope of curve = 15·64.

Valeramide.

40 c.c. *N*/2-valeramide. 40 c.c. *N*/2-NaOH. $Q = 2{\cdot}632$. $\alpha = 0{\cdot}8525$.

t.	$\sigma \times 10^3$.	$C \times 10^5$.	*K.*
87·50	78·61	23·58	3·32
125·0	77·34	23·03	3·31
157·2	76·54	22·60	3·18
178·0	75·71	22·35	3·15
333·0	71·61	20·60	3·01
374·0	70·41	20·13	3·04
395·5	69·88	19·91	3·03
449·0	68·73	19·40	3·02

Mean $K = 3{\cdot}13$

$\sigma^{0} = 0{\cdot}08186$, $\sigma^{0\cdot25} = 0{\cdot}06708$,
$\sigma^{0\cdot5} = 0{\cdot}05241$.

K calculated from slope of curve = 3·087.

Capronamide.

40 c.c. *N*/2 Capronamide. 40 c.c. *N*/2-NaOH. $Q = 12{\cdot}29$. $\alpha = 0{\cdot}8525$.

t.	$\sigma \times 10^3$.	$C \times 10^5$.	*K.*
75·38	69·86	20·06	14·75
93·50	68·23	19·36	14·62
103·92	67·13	18·90	14·59
111·75	66·32	18·58	14·55
148·42	63·22	17·17	14·44
174·50	61·25	16·30	14·36
188·55	60·22	15·83	14·42
230·66	57·67	14·65	14·38

Mean K = 14·51

$\sigma^{0} = 0{\cdot}07818$, $\sigma^{0\cdot25} = 0{\cdot}0666$, $\sigma^{0\cdot5} = 0{\cdot}05283$, $\sigma^{1} = 0{\cdot}02754$.

K calculated from slope of curve = 14·41.

Temperature = 95·9°.

Acetamide.

40 c.c. *N*/16 Acetamide. 40 c.c. *N*/16-NaOH. $a=0\cdot9326$.

t.	$\sigma\times10^3$.	$C\times10^6$.	*K*.
14·58	15·23	27·99	273·4
25·00	14·18	26·06	272·4
35·66	13·66	24·22	279·0
37·08	13·60	24·00	279·3
39·92	13·47	23·56	280·0
45·83	13·22	22·73	280·1
47·83	13·18	22·52	277·8
50·83	13·03	22·10	279·1
		Mean *K*=277·9	

$\sigma^0=0\cdot01571$, $\sigma^{0\cdot3}=0\cdot01264$.

Propionamide.

40 c.c. *N*/16 Propionamide. 40 c.c. *N*/16-NaOH. $a=0\cdot9326$.

t.	$\sigma\times10^3$.	$C\times10^6$.	*K*.
24·50	14·39	26·78	233·6
35·42	13·85	25·17	234·0
37·25	13·78	24·97	231·3
40·00	13·66	24·61	231·1
41·58	13·59	24·39	231·9
46·33	13·41	23·87	228·6
50·83	13·22	23·30	230·1
52·33	13·16	23·12	230·4
		Mean *K*=231·3	

$\sigma^0=0\cdot01588$, $\sigma^{0\cdot25}=0\cdot01327$.

Butyramide.

40 c.c. *N*/16 Butyramide. 40 c.c. *N*/16-NaOH. $a=0\cdot9326$.

t.	$\sigma\times10^3$.	$C\times10^5$.	*K*.
38·16	14·74	27·90	108·0
58·75	14·24	26·42	106·7
75·75	13·85	25·26	107·3
82·00	13·72	24·87	107·1
88·33	13·59	24·48	107·2
91·50	13·53	24·31	107·0
102·55	13·35	23·78	106·6
110·15	13·22	23·40	106·5
		Mean *K*=107·0	

$\sigma^0=0\cdot01588$, $\sigma^{0\cdot25}=0\cdot01323$.

iso*Butyramide.*

40 c.c. *N*/16 *iso*Butyramide. 40 c.c. *N*/16-NaOH. $a=0\cdot9326$.

t.	$\sigma\times10^3$.	$C\times10^5$.	*K*.
39·58	14·65	28·10	97·15
68·33	14·05	26·17	97·29
83·50	13·76	25·23	97·80
91·66	13·62	24·79	97·47
101·66	13·42	24·15	99·10
105·25	13·36	23·95	99·20
113·75	13·22	23·50	99·30
117·30	13·16	23·30	99·90
		Mean *K*=98·37	

$\sigma^0=0\cdot01563$, $\sigma^{0\cdot25}=0\cdot01320$.

Valeramide.

40 c.c. *N*/4 Valeramide. 40 c.c. *N*/4-NaOH. $a=0\cdot8698$.

t.	$\sigma\times10^3$.	$C\times10^5$.	*K*.
46·75	53·79	11·12	24·43
75·42	51·71	10·45	23·94
94·08	50·56	10·08	23·52
105·83	49·85	9·85	23·37
111·58	49·53	9·745	23·30
124·16	48·88	9·440	23·98
132·16	48·48	9·410	22·90
137·08	48·07	9·280	23·32
		Mean *K*=23·59	

$\sigma^0=0\cdot05806$, $\sigma^{0\cdot25}=0\cdot04837$-

Capronamide.

40 c.c. *N*/16 Capronamide. 40 c.c. *N*/16-NaOH. $a=0\cdot9326$.

t.	$\sigma\times10^3$.	$C\times10^6$.	*K*.
43·00	14·56	27·52	108·0
73·25	13·85	25·35	109·0
80·25	13·72	24·95	108·0
86·40	13·59	24·55	108·5
97·00	13·41	24·00	108·0
113·25	13·11	23·09	107·1
117·33	13·05	22·90	106·9
124·75	12·93	22·52	106·9
		Mean *K*=107·8	

$\sigma^0=0\cdot01578$, $\sigma^{0\cdot25}=0\cdot01322$.

These results are in contrast with those previously obtained in the case of hydrolysis by hydrochloric acid (*loc. cit.*).

When the amides are arranged in decreasing order of reactivity with respect to alkali, at constant temperature, this order is as follows:

formamide, acetamide, propionamide, capronamide, butyramide, *iso*butyramide, valeramide. The reactivity of formamide, as might be expected, is relatively great. That of valeramide, as in the case of hydrolysis by acid, is abnormally small, and this is the least reactive of the amides. The order of relative activity is, however, here reversed in the case of propionamide and acetamide, and also for butyramide and *iso*butyramide.

The velocities of hydrolysis of the amides by alkali under given conditions is greater than the rate of reaction with acid. Thus at 63·2° formamide is five times more reactive with respect to caustic soda than it is with acid, and propionamide is more than twice as reactive with soda than with acid.

The velocity-constants exhibit the usual large coefficients of variation with temperature. For example, acetamide is about thirty-one times as reactive at 95·9° as it is at 40·06. The temperature variations are expressed by the general formula:

$$\log_{10}K = \log_{10}K^0 + B\left(\frac{1}{T^0} - \frac{1}{T}\right) + C\left(\frac{1}{T^0} - \frac{1}{T}\right)^2.$$

The value of the constants for the amides investigated are given in the following table:

	Range.	T^0.	$\mathrm{Log}_{10}K^0$.	B.	$C \times 10^{-2}$.	B'.
Formamide	40·06—63·2	313·06	2·4870	3474	—	3474
Acetamide	40·06—95·9	,,	0·9565	3375	−6116	3173
Propionamide	,,	,,	0·9126	3346	−7043	3104
Butyramide.........	,,	,,	0·4778	3574	−7517	3318
*iso*Butyramide ...	,,	,,	0·4249	3702	−9457	3372
Valeramide	,,	,,	$\bar{1}$·6973	3763	−6107	3554
Capronamide	,,	,,	0·4867	2958	+5044	3136

In the last column is shown the mean differential coefficient B1 of the graph between the logarithm of the velocity-constant and the reciprocal of the absolute temperature for the range of temperature considered.

These values are much less than the corresponding values in the case of hydrolysis by acid. The following numbers show the agreement between the values computed from the formula and those read directly from the curves:

	T.	K (calc.).	K (curve).	T.	K (calc.).	K (curve).
Formamide............	333·9	1521	1503	322·6	6510	6486
Acetamide	334·0	40·46	40·55	357·9	161·7	161·5
Propionamide.........	,,	35·77	35·72	,,	137·5	136·5
Butyramide	,,	14·54	14·67	,,	61·24	61·10
*iso*Butyramide	,,	13·42	13·33	,,	56·81	56·50
Valeramide	,,	2·663	2·661	,,	12·73	12·56
Capronamide	,,	12·55	12·59	,,	56·30	56·87

This exponential variation of the reactivity with temperature is, as is well known, common to most reactions which have been investigated, and it will be of interest first to consider here the cause of this peculiar variation. An interesting explanation was advanced by Arrhenius (*Zeitschr. physikal. Chem.*, 1889, 4, 226) in a paper on the velocity of inversion of sucrose by acids. According to this view, a solution of sugar contains two forms in equilibrium. One of these is unstable and reactive and the other form is stable. The equilibrium between these forms is regulated by the equation:

$$C_a = KC_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_a and C_i are the concentrations of the active and inactive sugar respectively, and K is the equilibrium constant of the reaction. This leads to the relation:

$$\frac{d\log_e K}{d\theta} = \frac{q}{2\theta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for the variation of reactivity with temperature. In this formula q is the heat required to change 1 gram-molecule of "inactive" sugar to the "active" form, and this is equal to 25,600 calories. As a first approximation this quantity is a constant.

The application of this formula to other cases has proved its generality, and has justified the premises in the Arrhenius theory.

The question, however, arises as to the nature of the difference between these "active" and "inactive" forms. In the case of liquids and solutions "association" would give an adequate explanation. A dissolved substance may, for example, form complex molecules with the solvent, and equilibrium may be set up between the complex and the simple molecules. In the gaseous state, however, association of this kind is precluded, and some other hypothesis is needed. One is therefore led to the view that the explanation must rest on an atomic basis, and that the difference in property is to be accounted for by some modification, either in configuration or property, of the atom itself.

Regarded from the point of view of the electronic theory, the atom can exist in two conditions, an electrically neutral state, and a charged condition, due to the loss or gain of electrons. Thus, the mercury atom in mercuric chloride, or when in the ionic state in solution, is charged, that is, it has lost an electron; but under ordinary conditions the atom in uncharged. If, however, mercury vapour, which scarcely conducts electricity under ordinary conditions, is exposed to the Röntgen rays, it loses electrons and conducts readily (J. J. Thomson, *The Discharge of Electricity Through Gases*, p. 101). This indicates the change of the neutral atom to the charged condition. The existence of these two atomic states is tacitly assumed in current representations of oxidation, reduction, and ionisation. If, then, atoms can gain or lose electrons, it is very probable that electronic exchanges take place within the molecules of chemical substances, and this is sufficient to account for "active" and "inactive" forms of the same substance.

When combination of two atoms takes place, an electron passes from one atom to the other, with the result that the two atoms are equally and oppositely charged. The attractive force thus produced tends to make the molecule stable. This is the normal condition. If, however, the vibrational energy of the system becomes great enough, disturbance of the atomic equilibrium may take place and an electron may be forced back across the interatomic space, with consequent "depolarisation." The attractive force of atom for atom is thus diminished and the system becomes unstable and reactive. As the temperature is increased, the vibrational energy will become greater and the proportion of the "active" form will be increased. It is also clear that the ease with which depolarisation takes place will depend on the relative electrochemical character of the atoms concerned. Since strongly electropositive and electronegative elements respectively lose and gain electrons readily, molecules formed of elements differing greatly in electrochemical character would be generally stable, and unlikely to undergo such depolarisation under ordinary conditions. Also in such cases the temperature-coefficient of reactivity would be proportionally great. Conversely, under given conditions, depolarisation and electronic exchange would be expected to occur most readily in molecules where the constituent atoms are most nearly allied in electrochemical nature. If we assume that the change of inactive to active molecules is accompanied by a finite amount of heat-absorption equal to q calories per gram-molecule, then equation (2) will express the variation of the velocity-constant with temperature in the case of simple irreversible decomposition.

This result depends on the assumption that external energy can affect the intra-atomic energy, an assumption which appears to be justified by experiment.

The equilibrium between the two forms, as described above, is analogous to that existing in the case of tautomerism. In the latter case, difference of property is produced by the "wandering" of an atom, in the former by the movement of an electron.

These two forms may, for convenience, be termed "electromeric." The unstable reactive and stable forms will be referred to as the "depolarised" and "activised" forms respectively.

The principles stated in the foregoing may be summarised as follows:

(*a*) The decomposition of a non-ionisable polyatomic molecule into smaller parts is preceded by the "depolarisation" of those parts.

(*b*) Stable combination is preceded by the "activisation" of the interacting atoms or groups of atoms.

It will be noted that "depolarisation" of an atom or radicle in the sense employed above does not necessarily mean that the whole of the molecule or even of the atom becomes electrically neutral. Depolarisation need only necessarily occur between the atoms at which decomposition takes place, and, moreover, only at those parts of the atoms directly concerned in the decomposition.

This hypothesis would account satisfactorily for the difference between the two forms postulated by the Arrhenius theory. It is to be noted that if reaction takes place between several "depolarised" molecules, then the temperature-variation is expressed by:

$$\frac{d\log_e K}{d\theta} = \frac{q_1 + q_2 + \cdots}{R\theta^2} \quad . \quad . \quad (3)$$

where $q_1\ q_2 \ldots$ are the "heats of depolarisation" of the various interacting molecules.

According to this view the hydrolysis of acetamide by hydrochloric acid is represented as follows:

$$\mathrm{CH_3{\cdot}\overset{\circ}{C}O{\cdot}\overset{\circ}{N}H_2 + \overset{\circ}{H}{\cdot}\overset{\circ}{O}H + \overset{+}{H} + \overset{-}{Cl} = CH_3{\cdot}CO_2H + \overset{+}{N}H_4 + \overset{-}{Cl}}.$$

The symbol ○ serves to indicate the atoms between which depolarisation has occurred. Reaction here takes place between the "depolarised" amide and water molecules, the action of the acid being regarded as catalytic. If the effect of alkali on the rate of hydrolysis of acetamide is also catalytic, then the value of B' should be the same for both reactions. Reference, however, to the above results and also to those previously given (*loc. cit.*) for the case of hydrolysis by acid, shows that for all the amides investigated these factors are much less for the reaction of hydrolysis by alkali. Evidently, then, there is some essential difference between the two reactions. The same feature is recorded by Arrhenius (*loc. cit.*) with reference to the action of acid and alkali on ethyl acetate. The factor B' was shown to be greater for hydrolysis by acid, and the view was taken that this is due to the formation of a compound of the neutral salt with the ester, which is in equilibrium with two kinds of active ester, so that B' has here a modified meaning. If hydrolysis by alkali takes place as a result of the direct action of the hydroxyl ions on the non-electrolyte molecule, then another explanation is possible, since in this case B' is determined by the heats of "electromeric" change of the non-electrolyte molecule and possibly of the hydroxyl ion. Thus, the hydrolysis of acetamide by alkali on this view would be represented as follows:

$$\mathrm{CH_3{\cdot}\overset{\circ}{C}O{\cdot}\overset{\circ}{N}H_2 + \overset{-}{O}H = CH_3{\cdot}\overset{-}{CO}_2 + NH_3}.$$

On the other hand, there is evidence to show that in some cases of hydrolysis by alkali the action of the hydroxyl ions is catalytic. The decomposition of sodium chloroacetate by alkali is a case in point (Senter, Trans., 1907, 91, 473).

Further work in the direction indicated is, however, necessary and, with the object of elucidating the function of the acid and alkali, it is intended to extend the investigation to other reactions of hydrolysis.

CHEMICAL DEPARTMENT,
S.W. POLYTECHNIC INSTITUTE,
CHELSEA, S.W.

LXXXIX.—*Arsenic Di-iodide.*

By JOHN THEODORE HEWITT and THOMAS FIELD WINMILL.

SOME twenty-six years ago E. Bamberger and J. Philipp discovered that arsenic and iodine, besides uniting to form the ordinary tri-iodide, can also combine in the proportion of one atom of arsenic to two atoms of iodine (*Ber.*, 1881, **14**, 2643). Having established the composition and studied the solubilities and some reactions, they assigned to this substance the simplest possible formula AsI_2, and stated their intention of applying it to the synthesis of organo-arsenic compounds. No further work has appeared, and the substance has not apparently been examined by other chemists.

The present authors decided on a determination of the molecular weight with the intention, should the substance have the double formula As_2I_4, to use it, if possible, in conjunction with Grignard reagents in the synthesis of aromatic analogues of cacodyl. The formula As_2I_4 proved correct, but the substance is valueless as a synthetic agent, arsenic being liberated, and organic derivatives of arsine being produced.

Preparation and Formula.

The directions given by Bamberger and Philipp to heat arsenic with twice its weight of iodine in sealed tubes to 230° were usually followed, although we have obtained more certain results in preparing a product free from tri-iodide by employing a temperature of 260°. Recrystallisation from carbon disulphide was effected in an atmosphere of dry carbon dioxide, and the solution was driven from one vessel to another by a stream of the same gas. These conditions are essential, as the substance is very sensitive to moisture and oxygen, and the specimen used for analysis was dried in a current of carbon dioxide, the tubes in which it was preserved being also filled with the gas. In carrying out the analysis the substance was transferred from the weighing tube into a dilute solution of sodium carbonate, the free arsenic which separated was filtered off, the solution acidified with hydrochloric acid, and the remaining arsenic precipitated as sulphide. Iodine was estimated in a separate portion, the solution having been acidified with sulphuric acid:

$$\left.\begin{array}{l}0\cdot8044 \text{ gave } 0\cdot0347 \text{ As. } \quad \text{As}=4\cdot3. \\ \quad\text{and } 0\cdot2385\ As_2S_3. \quad \text{As}=18\cdot2.\end{array}\right\}\text{Total } 22\cdot5.$$

0·5704 gave 0·8099 AgI. I = 76·8.

As_2I_4 requires As = 22·8; I = 77·2 per cent.

The molecular weight was determined by the Landsberger boiling point method in carbon disulphide ($\Delta\tau = 23\cdot7$) solution:

0·5256 raised the boiling point of 13·83 CS_2 by 0·15°. M.W. = 601.
0·5768 „ „ 19·07 CS_2 by 0·125°. M.W. = 574.

As_2I_4 requires M.W. = 658 ($AsI_2 = 329$ and AsI_3 456).

The results, although not good, owing to the sensitiveness of the substance, leave no doubt as to the molecular weight.

Reactions.

Bamberger and Philipp already noted that when the substance was decomposed by water, the amount of arsenic liberated was less than that required by the equation

$$3As_2I_4 = 4AsI_3 + 2As.$$

The results obtained in our analysis of the compound confirm this observation.

Cold concentrated sulphuric acid is apparently without action, but some iodine is eliminated when the acid is raised to near its boiling point. Cold fuming nitric acid has apparently little immediate action, but, on heating, oxides of nitrogen and iodine vapour are given off, whilst eventually arsenic and iodic acids are produced.

Pyridine decomposes the substance immediately, arsenic is liberated, and arsenic tri-iodide passes into solution. The substance dissolves in boiling acetic anhydride; the material which separates on cooling is mostly yellow, but evidently not homogeneous. It is very probable that the greater portion of the product is a derivative of arsenic tri-iodide, since the solution of this substance in boiling acetic anhydride deposits beautiful orange crystals on cooling.

On adding one molecular proportion of finely-powdered arsenic di-iodide to an ethereal solution of four molecules of magnesium phenyl bromide, an oily substance, insoluble or sparingly soluble in ether, separated; as this was qualitatively shown to contain arsenic, halogen, and magnesium, it was probably an additive product. On decomposition with ice and dilute sulphuric acid, the ether dissolved an organic arsenic compound, which was deposited at first as an oil, on evaporating the ether. The oil having solidified, the product was crystallised from dilute alcohol, and colourless needles melting at 60° were obtained. The suspicion that the substance was merely triphenylarsine was confirmed by a mixed melting point with a specimen prepared by P. Pfeiffer and H. Pietsch's method (*Ber.*, 1904, **37**, 4621) from arsenic trichloride and magnesium phenyl bromide, the purity of which had been controlled by analysis:

0·2996 gave 0·1193 As_2S_3. As = 24·3.

$As(C_6H_5)_3$ requires As = 24·5 per cent.

It is evident that arsenic di-iodide can be of little use as a synthetic agent, the ease with which it furnishes the tri-iodide or its derivatives being prohibitive.

East London College.

XC.—*Separation of Cadmium from Zinc as Sulphide in the presence of Trichloroacetic Acid.*

By John Jacob Fox.

The usual quantitative methods of separating cadmium from zinc, other than electrolytic, depend on the use of mineral acids of strength sufficient to prevent the precipitation of zinc sulphide. The most convenient acids for this purpose are hydrochloric and sulphuric, but the quantity of these acids present must be limited to a maximum of about 1 gram of hydrogen chloride or 10 grams of sulphuric acid per 100 c.c. If these quantities are exceeded, some of the cadmium remains in solution and cannot be precipitated by hydrogen sulphide. Further, if the quantity of hydrogen chloride is less than 0·9 gram per 100 c.c., some zinc sulphide falls out of solution together with the cadmium sulphide. To ensure complete separation when much cadmium is present in a solution, three precipitations of the cadmium sulphide are necessary, and at the same time the amount of acid must be limited as mentioned above. For this purpose sulphuric acid is more convenient than hydrochloric, but there is considerable risk of keeping small amounts of cadmium in solution.

To avoid the inconvenience of several dissolutions and precipitations of the cadmium sulphide, an organic acid of the same order of strength as mineral acids was sought for, and finally trichloroacetic acid was selected. The strength of this acid as deduced from its degree of ionisation compared with hydrochloric acid, at a concentration of 1/32 normal, is in the ratio of about 1 to 1·08. This ratio approaches equality at greater dilutions, and it may be assumed that at much greater concentrations than 1/32 normal, trichloroacetic acid is still less dissociated than the corresponding equivalent of hydrochloric acid. The precipitation of zinc sulphide in presence of trichloroacetic acid bears this out. For if a solution containing about 1·0 gram of zinc and 6·1 grams of trichloroacetic acid per 100 c.c. is taken, a precipitate of zinc sulphide is formed on passing hydrogen sulphide, but the equivalent quantity of hydrochloric acid is sufficient under these conditions to prevent anything more than traces of zinc sulphide from being precipitated.

If, however, with the same concentration of zinc a solution is used containing 11 grams of trichloroacetic acid per 100 c.c., no precipitation of zinc sulphide results.

It is to be noticed in this connexion that the concentration of the zinc is also a determining factor in the precipitation of zinc sulphide. With solutions containing 0·1 gram of zinc per 100 c.c., as little as 4·5 grams of trichloroacetic acid, or 1 gram of hydrogen chloride, are sufficient to prevent the formation of zinc sulphide.

In general, concentrated solutions of trichloroacetic acid are not dissociated to the same extent as hydrochloric acid. This is of importance as regards the precipitation of cadmium sulphide, for strong solutions of trichloroacetic acid do not appear to exercise any effect in preventing the complete precipitation of cadmium sulphide, even when the concentration of the cadmium is small, as the following experiments show:

Volume of solution in c.c.	Grams of trichloroacetic acid present.	Gram of cadmium used.	Gram of cadmium obtained as cadmium sulphide.
15	6·70	0·0051	0·0050
55	16·74	0·0051	0·0050
105	33·48	0·0051	0·0050
200	34·12	0·1023	0·1024

To test the value of the reagent in the separation of zinc and cadmium, determinations were made on mixtures of solutions of zinc sulphate and cadmium chloride. It was found that when the proportion of zinc was large as compared with cadmium, and the concentration comparatively high, the separation of the two metals was not quite complete, owing to some zinc being carried down with the cadmium sulphide if the amount of the latter were more than a few milligrams. On redissolving and reprecipitating, a complete separation resulted in all the cases examined.

	Vol. of solution in c.c.	Grams of zinc present.	Gram of cadmium present.	Grams of trichloroacetic acid present.	Gram of cadmium obtained.
1.	120	1·240	0·0512	13·4	0·0512
2.	250	4·552	0·0512	67·0	0·0510
3.	100	1·138	0·0512	12·2	0·0507
4.	200	0·124	0·2236	28·6	0·2245
5.	150	0·0552	0·0466	15·0	0·0466

Experiments 1, 2, and 3 needed two precipitations, experiments 4 and 5 one only.

In the ordinary examination of metals for cadmium, the addition of trichloroacetic acid would be objectionable for the separation of the sulphides of Group II., since it might interfere with the complete precipitation of Group III. metals. To avoid this, the first partial separation of cadmium and zinc may be effected by using 1 gram of hydrogen chloride per 100 c.c. of solution. Some zinc sulphide will be precipitated together with the Group II. sulphides. The second separation can then be effected by adding to the neutral solution of zinc and cadmium an amount of trichloroacetic acid sufficient to give a solution containing at least 10 grams of this acid per 100 c.c. A large excess of trichloroacetic acid above 10 per cent. may be used without interfering with the precipitation of cadmium sulphide (see experiments above). The zinc may be precipitated in the filtrate from the cadmium sulphide by adding ammonia and ammonium sulphide, the presence of ammonium trichloroacetate being without effect on the precipitation of zinc sulphide.

Thus, 50 grams of crystallised zinc sulphate ($ZnSO_4,7H_2O$) corresponding to 11·380 grams of zinc, and 0·4128 gram of crystallised cadmium chloride ($CdCl_2,2H_2O$) corresponding to 0·2116 gram of cadmium, were dissolved in water and diluted to 350 c.c., there being 1 per cent. of hydrogen chloride present. The sulphide precipitate obtained was redissolved and neutralised; 17·3 grams of trichloroacetic acid were added, and the whole diluted to 100 c.c. The cadmium obtained as cadmium sulphide was 0·2119 gram, and the filtrate from this gave 0·1546 gram of zinc.

Similar results were obtained when trichloroacetic acid was used for both precipitations of cadmium sulphide, but when the amount of zinc present was small compared with the cadmium, one treatment was sufficient for practically complete separation of the two metals.

In some experiments it was found that when the concentration of trichloroacetic acid was high (50 per cent. and more) the cadmium was not immediately precipitated on passing hydrogen sulphide. The precipitation was readily started in such cases by the addition of a few drops of a dilute solution of ammonia.

GOVERNMENT LABORATORY.

XCI.—*Mixed Semi-ortho-oxalic Compounds.*

By G. DRUCE LANDER.

I HAVE previously shown (Trans., 1904, **85**, 984) that the primary diamido-semi-ortho-oxalic compounds, such as $CO_2Me{\cdot}C(NHPh)_2{\cdot}OMe$, described by Anschütz and Stiepel (*Annalen*, 1899, **306**, 5), do not exist, but that those reactions, which might be expected to produce them, yield amidino-oxalic esters, such as $CO_2Me{\cdot}C(NPh){\cdot}NHPh$.

In the present communication the mixed semi-ortho-compounds $CO_2Et{\cdot}C(OEt)_2{\cdot}NHPh$ and $CO_2Me{\cdot}C(OMe)_2{\cdot}NHPh$ are described. In constitution they bear the same relationship to the semi-*N*-phenylimino-oxalic esters, $CO_2R{\cdot}C(NPh){\cdot}OR$, as do Anschütz and Stiepel's supposed diamido-compounds to the amidino-esters. Contrary to anticipation, however, no genetic connexion can be shown to exist between the amidodialkyloxy-esters and the imino-ethers.

The new compounds were encountered during numerous unsuccessful attempts to prepare the oxalimino-ethers from the corresponding imide chlorides, $CO_2R{\cdot}CCl{:}NPh$, thus completing the synthetical relationships of the imino-ethers and amidino-esters with the parent oxanilates. The amide chloride, $CO_2Et{\cdot}CCl_2{\cdot}NHPh$, and the imide chloride, $CO_2Et{\cdot}CCl{:}NPh$, were described by Klinger (*Annalen*, 1877, **184**, 280). My failure to prepare the imino-ether from the imide chloride is chiefly due to the circumstance that I have never been able to prepare the imide chloride in sufficient quantity or purity for synthetical purposes, and having in other ways (Trans., *loc. cit.*) proved the non-existence of Anschütz and Stiepel's compounds, which was the primary object of the work, further attempts along this particular line have now been abandoned.

The amide and imide chlorides of the substituted oxamates possess interesting properties. For the type, the amide chlorides are exceptionally stable, first eliminating hydrogen chloride in the neighbourhood of 100°, thus,

$$CO_2Et{\cdot}CCl_2{\cdot}NHPh \longrightarrow CO_2Et{\cdot}CCl{:}NPh + HCl,$$

but this change is immediately succeeded by further decomposition, whereby, as Klinger noticed, ethyl chloride and carbon monoxide are formed. I find that the third main product is phenylcarbimide, the formation of which is readily demonstrable by its odour, and the production of diphenylcarbamide when treated with aniline or water. The behaviour on heating is thus elucidated as follows:

$$\mathrm{CO\,\vdots\,O\,\vdots\,Et\,\vdots{\cdot}C\,\vdots\,Cl\,\vdots{:}NPh \longrightarrow O{:}C{:}NPh + CO + EtCl.}$$

The amide chlorides of ethyl and of methyl oxanilates may be readily prepared by fusing together molecular proportions of the esters and phosphorus pentachloride, removing phosphoryl chloride by distillation in a partial vacuum below 70°, and crystallisation of the residue from a mixture of benzene and light petroleum. The *amide chloride* of *methyl oxanilate*, $\mathrm{CO_2Me{\cdot}CCl_2{\cdot}NHPh}$, has not been previously prepared. It forms, after one crystallisation, faint brown leaflets, or needles, melting at 100—103° and decomposing at about 150°.

The amide chlorides react normally with sodium alkyloxides, thus,

$$\mathrm{CO_2R{\cdot}CCl_2{\cdot}NHPh + 2NaOR = CO_2R{\cdot}C(OR)_2{\cdot}NHPh + 2NaCl,}$$

leading to the formation of the first representatives of the mixed semi-ortho-amido-compounds in which an NH group is present.

Semi-ortho-anilidotriethyl oxalate, $\mathrm{CO_2Et{\cdot}C(OEt)_2{\cdot}NHPh}$, results on adding the calculated amount of sodium dissolved in ethyl alcohol to the cold solution of the amide chloride of ethyl oxanilate in benzene. The reaction is speedily complete in the cold, and the organic product isolated by extraction of the benzene solution with warm water, desiccation, evaporation of the solvent, and distillation in a partial vacuum or crystallisation from dilute alcohol. From 20 grams of amide chloride 13·5 grams of the semi-ortho-oxalate were thus obtained in leaflets or needles melting at 69—70·5° and boiling at 172—174°/12 mm.:

0·1440 gave 0·3324 CO_2 and 0·1070 H_2O. C = 62·95; H = 8·25.
0·1358 „ 0·3132 CO_2 and 0·0973 H_2O. C = 62·90; H = 7·96.
0·1858 „ 8·6 c.c. moist nitrogen at 10° and 759 mm. N = 5·52.
$C_{14}H_{21}O_4N$ requires C = 62·92; H = 7·86; N = 5·24 per cent.

Determinations of methoxyl and of the molecular weight are given for the analogous methyl compound.

Semi-orthoanilidotrimethyl oxalate, $\mathrm{CO_2Me{\cdot}C(OMe)_2{\cdot}NHPh}$, is formed from the amide chloride of methyl oxanilate by the action of sodium methoxide in a manner entirely analogous to that just described for the ethyl compound. It forms colourless needles melting at 80—82° and boiling at 182°/20 mm.:

0·1455 gave 0·3120 CO_2 and 0·0878 H_2O. C = 54·48; H = 6·70.
0·1858 „ 10·1 c.c. moist nitrogen at 10° and 749 mm. N = 6·40.
0·1651 „ 0·5131 AgI. OMe = 41·00.
0·2153 in benzene gave $\Delta t = 0·401°$. M.W. = 223.
$C_{11}H_{15}O_4N$ requires C = 58·66; H = 6·66; N = 6·22; OMe = 41·30 per cent. M.W. = 225.

These data taken along with the mode of formation leave very little doubt that the compounds have the constitutions ascribed to them.

An attempt to obtain the compound $CO_2Et \cdot C(OMe)_2 \cdot NHPh$ by acting on $CO_2Et \cdot CCl_2 \cdot NHPh$ with sodium methoxide resulted in the production of a mixture of $CO_2Me \cdot C(OMe)_2 \cdot NHPh$ and

$$CO_2Et \cdot C(OMe)_2 \cdot NHPh$$

(compare Trans., *loc. cit.*, 989).

Transformations of the Semi-orthoanilido-oxalates.

The esters condense with aniline only on heating for some time at 200°, when diphenylamidino-oxanilide, $CO \cdot NHPh \cdot C\colon NPh \cdot NHPh$ (Klinger, *loc. cit.*; Trans., 1901, **79**, 700), and not the amidino-ester, $CO_2R \cdot C\colon NPh \cdot NHPh$, is formed.

It was not found possible to transform the ortho-esters by loss of alcohol into the corresponding semi-*N*-phenylimino-oxalic esters, although the change

$$CO_2R \cdot C(OR)_2 \cdot NHPh \longrightarrow CO_2R \cdot C(OR)\colon NPh + ROH$$

would *a priori* be deemed most likely.

As already indicated, the ortho-esters distil unaltered under low pressures, and when heated at the ordinary pressure they undergo the profound changes described later. It seemed likely that warming with acetic anhydride might effect the desired loss of alcohol. It does, but the imino-ether, which doubtless first results, is further decomposed by the acetic acid liberated in the reaction into oxanilate and acetic ester, for example:

$$CO_2Et \cdot C(OEt)\colon NPh + C_2H_4O_2 \longrightarrow CO_2Et \cdot CO \cdot NHPh + C_2H_3O_2 \cdot C_2H_5.$$

Neutralisation during the action by previously adding an excess of pyridine did not lead to the desired result.

When semi-orthoanilidotriethyl oxalate is heated in the oil-bath under the ordinary pressure, decomposition commences at 270°, accompanied by the distillation of a colourless liquid, and, towards the end of the action, of carbon monoxide. The liquid consisted for the most part of phenylcarbimide. In a partial vacuum a further oily fraction passed over between 140—160°/10 mm., in which no single product could be detected, but which possibly contained ethyl oxanilate, phenylurethane, and very small quantities of semi-*N*-phenyliminooxalicdiethyl ester. The residue in the flask did not distil at 270° and crystallised from alcohol in needles melting at 101—104°:

0·1530 gave 0·3768 CO_2 and 0·0815 H_2O. C = 67·16 ; H = 5·92.
0·1420 „ 0·3482 CO_2 „ 0·0752 H_2O. C = 66·87 ; H = 5·86.
0·1474 „ 10·8 c.c. moist nitrogen at 14° and 760 mm. N = 8·60.
$C_{19}H_{20}O_4N_2$ requires C = 67·05 ; H = 5·90 ; N = 8·23 per cent.

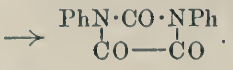
The methyl analogue is formed from semi-orthophenylamidotrimethyl oxalate under precisely similar conditions, and after two crystallisations from chloroform and methyl alcohol forms needles melting at 131—133°:

0·1370 gave 0·3278 CO_2 and 0·0754 H_2O. C = 65·25 ; H = 5·30.
0·1464 „ 11·4 c.c. moist nitrogen at 13° and 746 mm. N = 9·01.
0·2492 „ 0·3729 AgI. OMe = 19·74.
$C_{17}H_{16}O_4N_2$ requires C = 65·38 ; H = 5·12 ; N = 8·97 ; OMe = 19·87 per cent.

From the analyses and methoxyl estimations, which indicate two such groups, the compounds described above are formulated as $\mathrm{PhN{:}C(OEt){\cdot}NPh{\cdot}CO{\cdot}CO_2Et}$ and $\mathrm{PhN{:}C(OMe){\cdot}NPh{\cdot}CO{\cdot}CO_2Me}$, that is, as the *ethyl* and *methyl* iso*ethers* of *ethyl* and *methyl diphenyloxalurates* respectively.

Support is lent to this formulation from the circumstance that on hydrolysis of the ethyl compound with boiling hydrochloric acid, and of the methyl compound with boiling alcoholic hydrogen chloride, both yield diphenylparabanic acid, $\mathrm{CO(NPh{\cdot}CO)_2}$, thus:

$$\mathrm{PhN{:}C(OEt){\cdot}NPh{\cdot}CO{\cdot}CO_2Et} \longrightarrow \mathrm{PhNH{\cdot}CO{\cdot}NPh{\cdot}CO{\cdot}CO_2H}$$



$$\longrightarrow \begin{array}{c}\mathrm{PhN{\cdot}CO{\cdot}NPh}\\ \mathrm{|\qquad\quad |}\\ \mathrm{CO{-}{-}CO}\end{array} .$$

Royal Veterinary College,
London, N.W.

XCII.—*The Influence of Substitution in the Nucleus on the Rate of Oxidation of the Side-Chain. III. Oxidation of the Nitro- and Chloronitro-derivatives of Toluene.*

By Julius Berend Cohen and Henry James Hodsman.

In two former communications by Cohen and Miller (Trans., 1904, **85**, 174 and 1622), the influence of the halogens in determining the rate of oxidation of the side-chain was studied. The present paper contains an account of the oxidation of the nitro- and chloronitro-toluenes. The same method has been employed as that previously described (*loc. cit.*).

The following table contains the result of five series of experiments in which the isomeric compounds are arranged in the order of the quantity of acid formed, beginning with the least oxidised compound. For comparison the isomeric chlorobromotoluenes are added in the last column. The experimental details are given later.

Series I.	Series II.	Series III.	Series IV.	Series V.	
2 hours at 130—140°.	2½ hours at 130—144°.	4½ hours at 123—133°.	4 hours at 121—133°.	5 hours at 119—122°.	1¼ hours at 139—147°.
NO_2 : Cl.	NO_2 : Cl.	NO_2 : Cl.	NO_2 : Cl.	NO_2 : Cl.	Cl : Br.
2 : 3	2 : 3	2 : 3	—	2 : 3	3 : 5
2 : 5	2 : 5	2 : 5	—	2 : 5	2 : 5
2 : 6	2 : 6	2 : 6	—	2 : 6	2 : 6
3 : 6	3 : 5	*3 : 5	—	3 : 5	5 : 2
3 : 5	3 : 6	3 : 6	3 : 6	*—	2 : 3
3 : 2	3 : 2	3 : 2	*3 : 2	—	3 : 2
4 : 2	*4 : 2	4 : 3	4 : 2	—	4 : 2 and 2 : 4
4 : 3	4 : 3	4 : 2	4 : 3	—	4 : 3
*3 : 4	3 : 4	3 : 4	—	—	3 : 4

* Position of 4-chloro-2-nitrotoluene.

Excluding the 4-chloro-2-nitrotoluene, which occupies an exceptional position in the series and is considered later, the general result may be summarised as follows. The compounds with the nitro-group in the ortho-position are least oxidised, those with the nitro-group in the para-position are most oxidised, whilst the meta-compounds stand midway between the two. It follows therefore that the rate of oxidation is mainly dependent on the position of the nitro-group. This is confirmed by the result of oxidising the three nitrotoluenes, from which it will be seen that the same order is maintained.

* SERIES VI.—*Oxidation of the Nitrotoluenes.*

Time, ¾ hour. Temperature, 128—131°.

	Weight of acid.	Calculated as nitrotoluene.	M. p. of acid		†Weight of unchanged substance.	Total.
			Found.	Correct.		
Ortho	0·176	0·144	Very impure	147°	0·833	0·977
Meta	0·275	0·225	135—139°	140—141	0·760	0·985
Para.........	0·302	0·248	234—236	238	0·769	1·017

* In all series, the weight of each isomeride oxidised was 1 gram.

† The weight of unchanged substance was estimated merely as a check on the quantity of acid formed, but, owing to the volatility of the chloronitrotoluene, the values obtained cannot be regarded as very accurate.

On comparing the series of chloronitrotoluenes with the dihalogen derivatives it will be seen that they both agree as regards the para-substituted compounds (4 : 2, 2 : 4, 4 : 3, and 3 : 4), all of which are more easily oxidised than the other members of the series. It appears then that the rate of oxidation is to a great extent independent of the nature of the para-group present. In the case of the ortho- and meta-substituents, the meta-halogen in the dihalogen derivatives retards the oxidation the most, whereas in the nitro-halogen series it is the ortho-nitro-group which possesses this function. The result is that in the dihalogen compounds the dimeta-compound occupies the first place and is followed by a series of ortho-compounds, whereas in the nitro-halogen series the ortho-nitro-compounds stand first on the list and are followed by the meta-nitro-derivatives.

The position occupied by the 4-chloro-2-nitrotoluene fluctuates in a way which we found at first some difficulty in explaining. On examining the table on p. 971, it will be seen that the quantity oxidised appears to vary inversely with the length of time during which the substance is in contact with the oxidising agent. Now, if the acid first formed is rapidly attacked by the oxidising agent, continued action may result in its complete disintegration, accompanied by the elimination of chlorine as hydrochloric acid. If this is the case both the amount of acid formed and the total quantity of the products would show a low result. The following experiments were undertaken in order to elucidate these points. The estimation of free hydrochloric acid in the oxidised products was effected as follows.

The organic portion was extracted with ether from the contents of the tube and the aqueous layer drawn off. The ethereal layer was then washed with a little distilled water which was added to the aqueous portion already separated. An excess of *N*/10 silver nitrate was added, and, after filtering off the silver chloride, the excess was estimated with *N*/10 ammonium thiocyanate.

In the following table the effect of protracted oxidation on the nucleus of the 4-chloro-2-nitrotoluene is well marked. The amount

SERIES IV.—*Oxidation of the Chloronitrotoluenes.*

Time, 4 hours. Temperature, 121—133°.

NO_2 : Cl.	Weight of acid.	Calculated as chloronitrotoluene.	M. p. of acid.		Weight of unchanged substance.	Changed + unchanged substance.	Hydrochloric acid calculated as chloronitrotoluene.	Total.
			Found.	Correct.				
2 : 4	0·689	0·587	125—138°	140—143°	0·309	0·896	0·165	1·061*
4 : 2	0·702	0·597	135—142	142—144	0·328	0·925	0·005	0·930
3 : 2	0·691	0·588	175—180	179	0·326	0·914	0·009	0·923
3 : 6	0·613	0·547	150—160	165	0·405	0·952	0·003	0·955
4 : 3	0·704	0·599	135—140	185—186	0·307	0·906	0·011	0·917

* The excess over 1 gram of original substance must be placed to the account of unchanged substance which cannot be accurately estimated.

of hydrochloric acid set free is at least fifteen times greater than that derived from the other compounds of the series in which the nitro-group is not in the ortho-position.

This effect on the 4-chloro-2-nitrotoluene is shared by all the ortho-nitro-derivatives, for although they are less readily oxidised than the 4-chloro-2-nitro-compound, they all form hydrochloric acid and give a low total yield of products. The other isomerides not containing an ortho-nitro-group yield only comparatively small quantities of hydrochloric acid. The low yields from the ortho-nitro-compounds are shown in the following series (III).

SERIES III.—*Oxidation of the Chloronitrotoluenes.*

Time, 4½ hours. Temperature, 123—133°.

NO_2 : Cl.	Weight of acid formed.	Calculated as chloro-nitrotoluene.	M. p. of acid.		Weight of unchanged substance.	Total.
			Found.	Correct.		
2 : 4	0·572	0·487	125—138°	140—143°	0·194	0·681
2 : 6	0·513	0·437	120—155	161	0·318	0·755
2 : 3	0·421	0·358	170—220	235	0·448	0·806
2 : 5	0·456	0·387	115—130	137—138	0·429	0·816
3 : 2	0·855	0·728	175—180	179	0·149	0·877
4 : 3	0·859	0·731	155—163	185—186	0·170	0·901
3 : 5	0·774	0·659	145—150	148—149	0·261	0·920
4 : 2	0·887	0·755	138—143	142—144	0·177	0·932
3 : 6	0·825	0·702	150—158	165	0·266	0·968
3 : 4	1·055	0·898	165—180	178—180	0·076	0·974

The following table shows the amount of hydrochloric acid set free by the ortho-nitro-compounds compared with the 3 : 5 and 3 : 4 chloronitrotoluenes.

SERIES V.—*Oxidation of the Chloronitrotoluenes.*

Time, 5 hours. Temperature, 119—122°.

NO_2: Cl.	Weight of acid formed.	Calculated as chloronitrotoluene.	M. p. of acid.		Weight of unchanged substance.	Weight of changed + unchanged.	Hydrochloric acid calculated as chloronitrotoluene.	Total.
			Found.	Correct.				
2 : 3	0·185	0·157	180—220°	235°	0·696	0·853	0·046	0·899
2 : 5	0·220	0·187	115—130	137—138	0·747	0·933	0·049	0·982
2 : 6	0·258	0·219	130—155	161	0·697	0·916	0·055	0·971
2 : 4	0·440	0·374	120—135	140—143	0·524	0·898	0·099	0·997
3 : 5	0·289	0·246	140—146	148—149	0·722	0·968	0·010	0·978
3 : 4	0·729	0·620	165—175	178—180	0·359	0·979	0·009	0·988

The amount of chlorine set free from the nucleus appears to bear an approximately constant ratio to the quantity of substance oxidised as seen from the following table.

	NO_2 : Cl.	Weight of HCl calculated as chloronitrotoluene.	Weight of acid formed.	Ratio.
Series V	2 : 3	0·046	0·185	0·25
	2 : 5	0·049	0·220	0·22
	2 : 6	0·055	0·258	0·21
	2 : 4	0·099	0·440	0·22
Series IV	2 : 4	0·165	0·689	0·24

From this it appears probable that the action on the nucleus and on the side-chain are closely related, or, in other words, that the second change depends on the first.

EXPERIMENTAL.

Several of the compounds used in the foregoing experiments were prepared by special methods. The 3-chloro-2-nitrotoluene has not been previously described and was first obtained by one of us in conjunction with Mr. H. G. Bennett, so that all the ten isomeric chloronitrotoluenes are now known. In the preparation of the 5-chloro-2-nitrotoluene, Noelting and Stocklin's method (*Ber.*, 1891, **24**, 564) was found unsatisfactory and was accordingly modified.

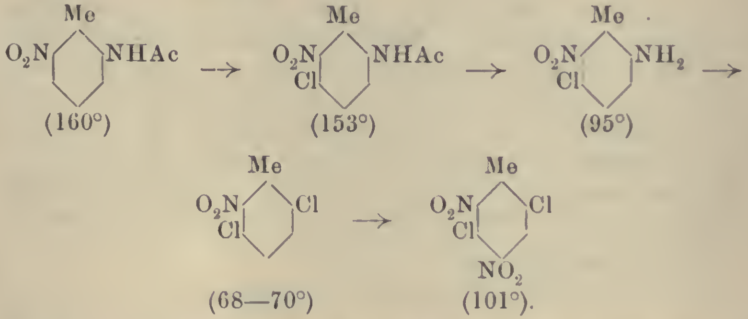
3-Chloro-2-nitrotoluene.—2 : 6-Dinitrotoluene was reduced to 2 : 6-nitrotoluidine in the usual way and the basic group acetylated. Ten grams of the nitroacetotoluidide were dissolved in 30 c.c. of hot glacial acetic acid, and dry chlorine was at once passed into the solution which was not allowed to cool. In this way chlorination proceeds without any crystallisation of the original substance. When the increase in weight roughly corresponded to the substitution of one atom of chlorine the process was stopped. After standing overnight, some of the chlorinated product usually separated out; otherwise crystallisation was hastened by cooling the solution in ice and salt. Those crystals, which were not very pure (m. p. 110—125°), were filtered off and a further quantity of chlorinated product was obtained as an oil by the addition of water to the filtrate. The oil partially solidified to a viscid mass from which the substance was obtained by repeated extraction with boiling water. The crude product was crystallised from alcohol and finally from water and melted at 150—152°. On analysis:

0·2607 gave 0·1610 AgCl. Cl = 15·28.

$C_9H_9O_3N_2Cl$ requires Cl = 15·54 per cent.

By heating the substance in a sealed tube with five times its weight of concentrated hydrochloric acid the acetyl group was removed, and the amino-group was then replaced by hydrogen by the usual method of diazotising in alcohol. The product was purified by draining it for several hours on a porous plate, cooled in ice, and then melted at

22—23°. The yields were very small. The constitution of the chloronitrotoluene was determined as follows. The acetyl derivative of the chloronitrotoluidine was hydrolysed and the amino-group replaced by chlorine. The product was then nitrated and gave a dichlorodinitrotoluene melting at 100—101°. Now, according to Cohen and Dakin (Trans., 1901, **79**, 1129, 1131) this melting point corresponds to the 2:5-dichlorodinitrotoluene and not to the 2:3-dichloro-compound, m.p. 71°, which is the only other likely product. The chlorine therefore enters the ortho-position to the nitro-group, the reactions taking place as follows:



The melting points of the different compounds are given with the respective formulæ.

In addition to the above, a dinitro-derivative of the chloronitrotoluene was prepared melting at 68—70° and a benzoyl derivative of the chloronitrotoluidine which melted at 212—213°.

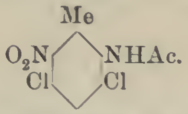
In the preparation of the chlorine derivative of the nitroacetotoluidide the process of chlorination should not be prolonged; otherwise a second hydrogen atom may be replaced by chlorine.

In one experiment 5 grams of the 2-nitro-6-acetotoluidide dissolved in 10 c.c. of hot glacial acetic acid were kept at 100° for five hours during which time dry chlorine was passed into the solution. The product was separated by cooling in ice and salt, and by adding a little alcohol. It was recrystallised from alcohol and melted at 195—197°:

0·3282 gave 0·3528 AgCl. Cl = 26·67.

$C_9H_8O_3N_2Cl_2$ requires Cl = 26·99 per cent.

The formula of the dichloro-compound is probably



5-Chloro-2-nitrotoluene.—*m*-Toluidine was acetylated with acetic anhydride and the product freed from the anhydride by allowing it to stand in contact with dilute sodium carbonate solution, for otherwise the subsequent nitration does not proceed smoothly.

To two parts of *m*-acetotoluidide dissolved in two parts of glacial acetic acid and eight parts of concentrated sulphuric acid cooled below 20°, one part of fuming nitric acid was gradually added, the temperature being kept at 5—10°. The nitro-group enters the para-position and, to a less extent, the ortho-position to the amino-group. The product was immediately poured into water, which precipitated the nitro-compounds.

The acetyl group was removed by heating the product on the water-bath with dilute sulphuric acid (1 vol. H_2SO_4 : 1 vol. water) until all had passed into solution. After neutralising the acid with sodium carbonate the base was distilled with steam to remove the 4-nitro-*m*-toluidine which is more volatile than the 2-nitro-compound. When the melting point of the distillate became constant, the residue was filtered, washed, and crystallised from alcohol (m. p. 135—138°).

The amino-group was replaced by chlorine, giving 5-chloro-2-nitrotoluene which was purified by distillation under reduced pressure:

0·2968 gave 0·2502 AgCl. Cl = 20·85.

$C_7H_8O_2NCl$ requires Cl = 20·69 per cent.

The remaining isomerides were obtained by well-known methods.

Details of the results obtained by the oxidation of Series I and II of the chloronitrotoluenes are given in the following tables.

Series I.—*Oxidation of the Chloronitrotoluenes.*

Time, 2 hours. Temperature, 130—140°.

NO_2 : Cl.	Acid formed.	Calculated as chloronitrotoluene.	M. p. of acid.		Unchanged substance.	Total.
			Found.	Correct.		
2 : 3	0·111	0·095	180—195°	235°	0·873	0·968
3 : 2	0·286	0·243	175—180	179	0·655	0·898
2 : 4	0·314	0·267	125—135	140—143	0·668	0·935
4 : 2	0·288	0·245	135—140	142—144	0·782	1·027
2 : 5	0·132	0·112	122—132	137—138	0·836	0·948
5 : 2	0·211	0·180	155—161	165	0·812	0·992
2 : 6	0·160	0·136	140—155	161	0·828	0·964
3 : 4	0·534	0·454	175—180	185	0·515	0·969
4 : 3	0·296	0·252	137—141	178—180	0·719	0·971
3 : 5	0·213	0·181	145—148	148—149	0·812	0·993

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